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WATER TREATMENT BY MEMBRANE ULTRA-FILTRATION

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WATER TREATMENT BY MEMBRANE ULTRAFILTRATION

By

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27 Abstract

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The presence of low concentrations of surface active agents in aqueous ultrafiltration feeds significantly reduced the steady-state trans-membrane flux. The nonionic surfactant and the anionic surfactant interacted with a polysalt membrane, causing maximum flux reductions of 24% and 20% respectively. The nonionic surfactant interacted with a cellulose acetate membrane, causing a maximum flux decline of 25%. The smallest flux reduction, of the order of 5%, was observed for the anionic surfactant interacting with the cellulose acetate membrane. In all but one case the distilled water flux returned to its original value consequent to a distilled water rinse following ultrafiltration in the presence of surface-active solute.

There was essentially no observable flux decline associated with the ultrafiltration of Carbowax 600 solutions with the cellulose acetate membrane. A 5% flux reduction was observed during ultrafiltration experiments on these same solutions with the polysalt complex membrane.

These composite results suggest that at least for the specific systems studied, solute asymmetry and in turn surface activity contributes specifically to flux-limiting membrane interactions.

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ABSTRACT

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SECTION I

CONCLUSIONS

1. The presence of trace concentrations of surface-active agents (surfactants) in aqueous ultrafiltration feeds significantly reduced the trans-membrane flux. There was a negligible flux reduction associated with the addition of a similar but non-surface active solute, polyethylene glycol (Carbowax 600), to the ultrafiltration feed.

2. Both the nonionic surfactant, polyoxyethylene-octylphenol (Triton X-100), and the anionic surfactant, sodium dodecylbenzene-sulfonate (SDBS), interacted with the polysalt membrane, causing maximum flux reductions of 24% and 20% respectively. Triton X-100 interacted with the nonionic, asymmetric cellulose acetate membrane, causing a maximum flux decline of 25%. The percentage drop in flux associated with these interactions either remained constant or increased slightly as the trans-membrane pressure drop increased. The smallest flux reduction, of the order of 5%, was observed for the SDBS - cellulose acetate membrane combination.

3. The nonsurfactant, Carbowax 600, in combination with the cellulose acetate membrane caused no flux reductions. The 100 ppm Carbowax 600 solution actually caused a slight flux increase over the flux for distilled water. When ultrafiltered by the polysalt membrane, the Carbowax 600 solutions caused a slight flux decline (a maximum decline of 8%).

4. Since the addition of Carbowax 600 to a distilled water feed caused no flux reduction for the cellulose acetate membrane, flux reductions deriving from the addition of Triton X-100 may be attributed to solute-membrane interactions as a result of specific surface activity.

5. In all but two cases the flux of distilled water returned to its original value consequent to a distilled water rinse following solute ultrafiltration. These data suggest that the solute-membrane interactions are transient and largely confined to the membrane surface.

6. The trans-membrane flux for both membranes dropped as the bulk solute concentration of either surfactant increased. In the case of the 1000 ppm Triton X-100-polysalt membrane combination at 100 psi, the flux appeared to become pressure independent consistent with gel formation at the upstream membrane surface.

7. In general, solute rejection was better than 90% for all combinations of membrane composition and solute type.

8. In most cases, there was little or no change in solute retention as the solute concentration or the trans-membrane pressure drop increased.

9. The increased rejection for 1000 ppm of Triton X-100 compared with 100 ppm may be a consequence of micelle formation at Triton X-100 concentrations exceeding 100 ppm. The micelles would be totally rejected by the membrane, resulting in a much higher apparent rejection of the surface-active solute. For Carbowax 600, solute rejection decreased as the solute concentration increased from 100 ppm to 1000 ppm. Since Carbowax 600 does not form micelles, this result is consistent with the suggested effect of micelle formation.

SECTION II

RECOMMENDATIONS

1. A program utilizing the present test loop for the ultrafiltration of multicomponent aqueous solutions would be a logical extension of the present work. Solute systems could include combinations of micro-solutes (salts), macrosolutes, and surfactants. Interactions related to trans-membrane flux and solute rejection would be studied.

2. Future work to evaluate the effect of upstream solution flow rate over the membrane surface on both the trans-membrane flux and the solute rejection is recommended.

3. Future work to evaluate more completely the effect of solute concentration on both the trans-membrane flux and the solute rejection is recommended.

SECTION III

INTRODUCTION

Classically the separation processes of the chemical industry involve contacting "natural" phases and effecting an enrichment of a desired component in one phase. Examples are crystallization (solid-liquid), distillation, absorption (vapor-liquid), extraction (liquid-liquid), and flotation (solid-liquid-vapor). Recently, difficult separations which were economically or technologically prohibitive have been effected by contacting the multicomponent phase with a synthetic phase. Examples are ion exchange, gaseous diffusion, chromatography, gel permeation chromatography, and the broad class of separations which are effected by "membrane processes."

Reid, et al. in 1959 showed cellulose acetate to be an effective membrane material for water desalination by reverse osmosis, even though the early membranes possessed low permeabilities. It was not until Loeb, et al. in 1960 improved permeabilities of these cellulose acetate membranes by altering the casting technique to produce an anisotropic membrane that reverse osmosis acquired importance, first as a desalination technique and later as a general unit operation for concentration, separation, and fractionation of solutions. The fantastic implication of their advance was that membrane separation as a potential unit operation of the chemical industry need not be applied to purification of high priced end products, but could also be used competitively on the cheapest of industrial products - potable water. Since this development, a broad range of membrane types have been fabricated from a variety of polymeric materials with a wide spectrum of separation characteristics. Through careful selection of components, membranes have been produced with excellent resistance to thermal and chemical attack with sufficient mechanical strength to withstand conditions of industrial operation. The anisotropic (asymmetric) membrane makes possible a high hydraulic permeability combined with rejection of quite small solute molecules at reasonable pressures.

Processes similar to reverse osmosis more properly termed ultrafiltration and permselective transport are developing at an accelerated pace as a result of the reverse osmosis desalination success. Ultrafiltration is a process for separation, concentration, and fractionation of macromolecular solutions. The high molecular weights of the solutes insure the existence of a relatively low osmotic pressure gradient, so that unlike reverse osmosis of microsolute-containing solutions, only moderate operating pressures are required. Since 1965 there have been applications of ultrafiltration in food concentration, sewage treatment, industrial pollution abatement, and biomedical research.

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All of the diverse processes previously mentioned have several features in common:

(1) The technological success of the process depends in large part on a membrane whose transport properties are specifically tailored to the separation in question. High specific flux rates and high selectivity are required.

(2) Economic success depends additionally on a stable membrane and a device which maximizes membrane area per unit equipment volume.

(3) The process should be continuous to handle the mammoth volumes ordinarily encountered in the production of inexpensive products and by-products.

(4) Due in part to the high permeability of these membranes, prohibitive accumulation of rejected solutes at the upstream membrane surface frequently occurs. This concentration polarization reduces the efficiency of the process by limiting the trans-membrane flux and must be minimized by the expenditure of mechanical energy to reduce the thickness of the boundary layer.

Applications

Reverse osmosis was first applied to desalination and has since become a major tool for water demineralization (Nusbaum, Cruver, and Sleigh, 1972). With salt concentrations found in brackish water, reverse osmosis is a very effective separation process; however, when extended to salt concentrations of the seawater range, more limited success has been met (Keilen and DeHaven, 1965; Miller, 1968).

Perhaps the most promising yet least investigated application of reverse osmosis and ultrafiltration involves the treatment of aqueous wastes from both municipal and industrial sources (Nusbaum, Cruver, and Sleigh, 1972). Pollution of water supplies within the food industry is a significant problem, since many food wastes possess an extremely high BOD requirement. In the potato starch industry, waste effluent containing valuable proteins, free amino acids, organic acids, and sugars can be processed by ultrafiltration. Reclamation of these materials, which are highly resistant to biodegradation, could provide an economic solution to this waste removal problem (Porter, Siciliano, Krulick, and Heisler, 1970). Ultrafiltration has been used to obtain a high-protein meal by concentrating crude protein obtained from meat wastes (work performed by the Amicon Corporation). Yeasts which are high in protein and vitamin content can be removed from beer by ultrafiltration, eliminating the need for pasteurization. In the dairy industry increasingly stringent pollution controls have made the discharge of whey as a liquid waste a critical problem. This disposed whey contains as much as 70% of the nutritive value of milk. By ultrafiltration whey

protein may be concentrated without thermal denaturation for use as an animal or human protein supplement (Porter and Michaels, 1971). Again as in most applications of membrane processes, serious production limitations result from the flux-limiting concentration polarization of rejected solutes.

Limitations of Reverse Osmosis and Ultrafiltration

Applications of present reverse osmosis and ultrafiltration systems must be conducted within several limitations as presented by Nusbaum, et al. (1972).

(1) For normal long term applications of cellulose acetate membranes, pH limits are 3 to 8. Vos, Burris and Riley (1966) reported minimum hydrolysis rates for cellulose acetate between pH 4 and 5 with rapid deterioration occuring above pH 7.0 or below 2.5. For the polysalt membranes, recommended applications are for systems with pH below 12, HCl and HNO_3 concentrations below 10%, and other acid concentrations below 5% (Amicon Corporation, 1971).

(2) The preferred temperature range for the application of cellulose acetate membranes is between 65 and 85°F, with minimum hydrolysis at 73°F (Vos, Hatcher and Merten, 1966). Higher temperatures increase the rate of cellulose acetate hydrolysis, while lower temperatures eliminate hydrolysis but reduce the trans-membrane flux. Operation below 122°F is recommended for use of polysalt membranes, with the attendent problem of reduced flux at lower temperatures (Amicon Corporation, 1971).

(3) Organics of low molecular weights exhibit poor rejections with the cellulose acetate membrane. The retentivity of the polysalt membrane is a function of the solute molecular configuration, but usually correlates well with the solute molecular weight. Polysalt membranes are available with increasing degrees of "tightness" a term used to denote the molecular weight above which a solute will be rejected.

(4) Some materials, including strong oxidizing agents, solvents, and other organic compounds, cause dissolution of the cellulose acetate membrane. Similarly, for the polysalt membrane problems result with solutions of waste immiscible solvents, phenols, and strongly ionic surfactants and detergents (Amicon Corporation, 1971).

(5) Solutions of high viscosity are difficult to treat with any membrane system.

(6) It is possible that the membrane or material adhering to it can serve as a nutrient for some bacteria; thus, cleaning must be supplemented with bactericidal agents which do not damage the membrane

(Kissinger and Willits, 1970).

(7) Some concentrated solutions may possess large osmotic pressures which exceed feasible operating pressures.

(8) Solutions possessing solutes that concentrate at the membrane surface will cause flux-limiting concentration polarization.

Mechanisms of Membrane Transport

Transport models describing solvent and solute transport within the membrane for both reverse osmosis and ultrafiltration may in general be divided into two basic categories, the viscous-flow model and the solution-diffusion model (Michaels, 1968).

(1) Viscous-Flow Model. Solvent in viscous flow moves through membrane micropores, carrying solute molecules through those pores whose dimensions are large enough to allow their passage. Selectivity is almost entirely due to a sieving mechanism.

In ultrafiltration Michaels (1968) and Blatt, et al. (1970) found that transport in microporous ("loose") membranes, which by definition retain macrosolutes of molecular weights>500 or molecular dimensions 10>Å, is described by a viscous-flow model. For such membranes the simplified transport relationships are, for the solvent:

$$J_1 = \frac{\bar{P}_1}{t_m} \Delta P \qquad (1)$$

where

J_1 = trans-membrane solvent flux ($ml/cm^2 \cdot sec$)

$\bar{P}_1$ = membrane permeability constant for the solvent ($ml/cm \cdot sec \cdot psi$)

t_m = membrane thickness (cm)

ΔP = trans-membrane pressure drop (psi)

and, for the solute:

$$J_2 = C_b (1 - \sigma) J_1 \qquad (2)$$

where

J_2 = trans-membrane solute flux ($ml/cm^2 \cdot sec$)

C_b = solute concentration in the bulk upstream solution (g/cm^3)

σ = solute rejection coefficient

The continuity constraint requires, however, that

$$J_2 = C_p J_1 \tag{3}$$

where

C_p = solute concentration in the permeate (g/cm^3)

Therefore

$$\sigma = 1 - \frac{C_p}{C_b} \tag{4}$$

Since σ is determined solely by solute molecular dimensions and the membrane pore size distribution, solute rejection for a sieve-type membrane is independent of the trans-membrane pressure drop.

(2) Solution-Diffusion Model. Both the solvent and solute independently dissolve in the membrane and transfer across it by molecular diffusion, driven by concentration gradients established by the trans-membrane pressure drop. Selectivity is due to the different permeabilities of the membrane to solvent and solute.

In ultrafiltration Michaels (1968) and Blatt, et al. (1970) found that transport in diffusive ("tight") membranes, which retain microsolutes of molecular weight < 500 or molecular dimensions < 10 Å, is described by this second model. For these diffusive-type membranes, the simplified transport relationships are, for the solvent:

$$J_1 = \frac{\bar{P}_1}{t_m}(\Delta P - \Delta\pi) = \frac{\bar{C}_1 D_1 \bar{V}_1}{t_m RT \rho_1}(\Delta P - \Delta\pi) \tag{5}$$

where

$\Delta\pi$ = solute osmotic pressure difference between the bulk upstream solution and the permeate solution (psi)

$\bar{C}_1$ = mean concentration of solvent in the membrane (g/cm^3)

D_1 = solvent diffusion coefficient in the membrane (cm^2/sec)

$\bar{V}_1$ = partial molar volume of solvent in the solution ($cm^3/mole$)

R = gas constant ($psi \cdot cm^3/mole \cdot {}^oK$)

T = absolute temperature (^oK)

ρ_1 = density of solvent (g/ml)

for the solute:

$$J_2 = \frac{k_2 D_2}{t_m} (C_b - C_p) = \frac{\bar{P}_2}{t_m} (C_b - C_p) \tag{6}$$

where

k_2 = solute distribution coefficient between the membrane and the solution ($ml/psi \cdot cm^3$)

D_2 = solute diffusion coefficient in the membrane (cm^2/sec)

$\bar{P}_2$ = membrane permeability constant for the solute ($ml/cm \cdot sec \cdot psi$)

The continuity constraint further requires

$$J_2 = C_p J_1 \tag{7}$$

The simultaneous solution of Eqs. (5) to (7) yields

$$\sigma = 1 - \frac{C_p}{C_b} = \frac{(\bar{P}_1/\bar{P}_2) \cdot (\Delta P - \Delta\pi)}{1 + (\bar{P}_1/\bar{P}_2) \cdot (\Delta P - \Delta\pi)} \tag{8}$$

The rejection coefficient is dependent on the trans-membrane pressure drop as well as the relative permeabilities of the solvent and solute in the membrane. In practice the solvent flux is not quite linear in $(\Delta P - \Delta\pi)$ because of postulated membrane compaction at higher trans-membrane pressure drops. No real diffusive membrane permits completely independent solvent and solute flow. Because of this coupling, both the solvent and solute permeabilities are slightly pressure dependent (Michaels, 1968).

Flux-Limiting Phenomena

Decreased process efficiency caused by flux-limiting concentration polarization can severely limit the economic feasibility of ultrafiltration. As suggested by Porter and Michaels (1971), membrane life is limited primarily by fouling rather than mechanical breakdown. Michaels, et al. (1965) investigated membrane permeation rates and rejection coefficients associated with the presence of polyvinylmethylether in a saline feed. It was found that the addition of a small amount of this substance at any trans-membrane pressure drop significantly improved the salt retention of a cellulose acetate membrane with only a slight decrease in the trans-membrane water flux. The polyvinylmethylether treatment also reduced the pressure dependency of the trans-membrane salt flux. These effects were attributed to a physical blockage of the larger pores by the large polymer molecules. While these blocked pores restricted flow of the saline solution, movement of ions in the remaining membrane matrix could still occur by normal diffusive transport.

More recently Kesting, Subcasky, and Paton (1968) reported the same effects of additives including surfactants on salt rejection but found significant trans-membrane water flux reductions associated with the addition of small amounts of certain additives. The addition of 43 ppm (parts per million by weight) of polyoxyethylenenonylphenol (N=9) to a 1% NaCl solution processed at a trans-membrane pressure drop of 54.4 atm, a temperature of 25°C, and a bulk solution flow velocity of 100 cm/sec caused a 15% reduction in the water flux and a 48% reduction in the salt flux. The authors postulated the formation of a "liquid-state membrane" at the interface between the cellulose acetate membrane and the saline solution, which acted in series with the membrane to provide an additional selective resistance to mass transfer. At low additive concentrations this layer was incomplete, but at or above the critical micelle concentration of the additive the layer was assumed to cover the membrane surface completely. The major reductions in both salt and water transport occurred before the critical micelle concentration was reached. At additive concentrations in excess of the critical micelle concentration, minor changes in the trans-membrane transport were attributed to compaction of the fully developed additive layer as more molecules tried to become oriented at the surface. Kesting noted considerable variation in the permeability and selectivity of different additive layers. The effectiveness of the layer in improving the selectivity of the underlying membrane increased with increasing hydrophilicity (increasing hydrophilic/hydrophobic ratio) of the additive, and was believed to be related to the capacities of various additives for binding water, since water permeation is proportional to the number of hydrophilic sites available for hydrogen bonding. Polyvinylmethylether and surfactants such as polyoxyethylenenonylphenols which strongly bind water were found to increase the salt-rejecting capacity of the underlying cellulose acetate membranes, while surfactants like sodium dodecylsulfate which do not bind water were ineffectual

in this respect.

Using an ABCOR HFA-100^R membrane, Short, Skrinde, and Newton (1970) studied membrane permeation rates and rejection coefficients associated with the presence of nonionic surfactants in feeds containing raffinose. Although these surfactants had relatively high hydrophilicity, they had no discernable effect on the trans-membrane water flux and did not alter the raffinose rejection. With the pure surfactant nonylphenoxy-polyethyleneoxyethanol (N=20), the rejection showed a slight decrease followed by a slight increase as the surfactant concentration increased. The addition of 0.5% raffinose improved surfactant rejection from approximately 40% to about 50%. The investigators attributed their seemingly anomalous results to a modification of the molecular bonding in the surfactant layer caused by the raffinose.

These studies all appear to indicate the presence of surfactant layers or deposits on the membrane surface at low bulk surfactant concentrations. These layers can alter both the permeation rates and the rejection coefficients of the underlying membrane, to an extent that depends on the surfactant type (possibly the hydrophilic/hydrophobic ratio) and on the characteristics of other solutes present in the feed solution.

The Effect of Concentration Polarization on Transport within the Membrane

Concentration polarization always reduces the trans-membrane flux and the solute-retention efficiency within both microposous (loose) and diffusive (tight) membranes. When concentration polarization occurs at the upstream membrane surface, the solute concentration at this surface is significantly higher than it is in the upstream bulk solution. For this case, Blatt, et al. (1970) predicted the effect on membrane transport in terms of the concentration polarization modulus (the ratio of solute concentration at the upstream membrane surface to its concentration in the upstream bulk solution) for both types of membranes.

(1) Microporous (Loose) Membranes. When the membrane is neither completely retentive nor completely permeable to solute, solute rejection shows concentration-dependent effects. Usually for solutions containing at least a few weight percent solute, the trans-membrane solvent flux decreases slightly with increasing bulk solute concentration, while the solute rejection increases. The viscous drag exerted by solute molecules in the membrane micropores that allow their passage increases as the solute concentration at the upstream membrane surface increases. This drag reduces flow in the pores that contain solute, while favoring flow in the smaller pores where solute is absent. As a consequence, solute rejection is increased while solvent transfer is altered only slightly. The membrane transport relations, given previously by Eqs. (1) to (4), become in the presence of concentration polarization (for $C_p << C_b$) for the solvent:

$$J_1 = \frac{\bar{P}_1}{t_m} \Delta P \tag{9}$$

for the solute:

$$J_2 = MC_b(1 - \sigma)J_1 \tag{10}$$

where

M = concentration polarization modulus

$$M = \frac{C_w}{C_b} \tag{10a}$$

The continuity constraint requires

$$J_2 = C_p J_1 \tag{11}$$

Therefore

$$\sigma = 1 - \frac{C_p}{MC_b} = 1 - \frac{C_p}{C_w} \tag{12}$$

or

$$\sigma_A = 1 - \frac{C_p}{C_b} = 1 - M(1 - \sigma) \tag{13}$$

where

σ_A = apparent solute rejection coefficient

(2) Diffusive (Tight) Membranes. As the concentration polarization modulus increases, the solvent trans-membrane flux is reduced according to Eq. (5) because of an increase in $\Delta\pi$. Since the solute concentration at the upstream membrane surface is increased, the solute flux through the membrane is in turn increased according to Eq. (6). As a result of the increases in both $\Delta\pi$ and the solute concentration at the upstream membrane surface, the solute rejection given by Eq. (8) declines. The membrane transport relations, given previously by Eqs. (5) to (8) become in the presence of concentration polarization (for $C_p << C_b$) for the solvent:

$$J_1 = \frac{\bar{P}_1}{t_m} (\Delta P - M\Delta\pi) \tag{14}$$

for the solute:

$$J_2 = \frac{\bar{P}_2}{t_m} (MC_b - C_p) \tag{15}$$

The continuity constraint requires

$$J_2 = C_p J_1 \tag{16}$$

Therefore by simultaneous solution of Eqs. (14) to (16)

$$\sigma_A = 1 - \frac{C_p}{C_b}$$

$$\sigma_A = 1 - \frac{M}{1 + (\bar{P}_1/\bar{P}_2)\cdot(\Delta P - M\Delta\pi)} \tag{17}$$

Transport processes occurring in the concentration polarization region adjacent to the upstream membrane surface, which have nothing to do with transport within the membrane, usually so strongly dominate the ultrafiltration process that they negate the importance of the membrane transport effects previously mentioned (Blatt, Dravid, Michaels and Nelsen, 1970).

Mechanisms of Transport in the Concentration Polarization Region

Brian (1966) developed for reverse osmosis a fundamental analysis of mass transfer in the liquid phase adjacent to the membrane upstream surface. This analysis was later extended to ultrafiltration by Michaels (1968). Several investigators have developed comprehensive analytical models for concentration polarization in reverse osmosis (Brian, 1965; Gill, Zeh and Tien, 1966; Kimura and Sourirajan, 1968a; Kimura and Sourirajan, 1968b; Merten, Lonsdale and Riley, 1965; Sherwood, Brian and Fisher, 1964; Sherwood, Brian, Fisher and Dresner, 1965; Sourirajan, 1970) and ultrafiltration (Blatt, Dravid, Michaels and Nelsen, 1970; deFilippi and Goldsmith, 1970). A recent review by Gill, Derzansky and Doshi (1971) outlined a number of mathematical models and solutions describing concentration polarization for various geometries and membrane parameters in both laminar and turbulent flow.

Blatt and co-workers (1970) have used the results of many investigators to construct transport models for solutions of microsolutes and macrosolutes. These models can be used to predict the effects of concentration polarization on trans-membrane flux and solute rejection.

(1) Concentration Polarization Model for Macrosolutes (Gel Model). The model of Blatt, et al. (1970) for macrosolute ultrafiltration, referred to as the gel model, postulates the existence of one or two layers adjacent to the membrane which account for the principal resistance to mass transfer in the upstream solution. The first layer, termed the concentration or polarization boundary layer, is of a hydrodynamic nature, and extends from the bulk fluid phase to the second layer if it is present, otherwise to the membrane suface. The second layer, more physical in nature and termed the gel layer, arises from a buildup or caking of solute on the membrane surface. In the remainder of this section, the principal results and predictions of Blatt's model are outlined.

At the outset of ultrafiltration, solute rejection by the membrane causes the solute concentration at the membrane surface to rise from its value C_b in the bulk fluid to a value $C_w > C_b$, and the resulting concentration gradient across the concentration boundary layer gives rise to back-diffusion of solute. C_w continues to increase until a steady-state is reached in which the rate of solute convection to the membrane equals the sum of the back-diffusion rate and the membrane permeation rate. If the convective flux to the membrane increases (due, for example, to an increase in the trans-membrane pressure drop), the solute concentration at the membrane C_w again rises until the back-diffusion rate again balances the increased rate of convection. This state, in which a single boundary layer exists and the solute concentration at the membrane-boundary layer interface is a function of the convective flux, is termed the "pre-gel-polarized region."

The second state of the model occurs if the concentration C_w reaches a limiting value C_g, at which gel-formation (or more precisely, some form of solute caking) occurs. Once this state is attained, a further increase in the convective flux serves only to increase the thickness of the gel layer adjacent to the membrane, with the concentration at the gel layer-concentration boundary layer interface remaining constant at C_g. This two-layer state is referred to as the "gel-polarized region."

The relationship between the convective flux and the steady-state concentrations at the limits of the boundary layer is obtained from a solute mass balance for this layer by making the following additional assumptions:

(1) the rate of solute permeation through the membrane or gel layer is negligible compared to the rates of convection to and from the interface;

(2) the thickness of the concentration boundary layer, δ, and the solute diffusivity within this layer, D_s, are independent of convection rates and the absence or presence of a gel layer.

Under these conditions, the solute continuity equation and its boundary conditions are

$$J_1 \frac{dC_2}{dX} - D_s \frac{d^2C_2}{dX^2} = 0 \qquad (18)$$

$$X = 0 \qquad C_2(X) = C_b \qquad (18a)$$

$$X = \delta \qquad J_1 C_2(X) - D_s \frac{dC_2(X)}{dX} = 0 \qquad (18b)$$

where

J_1 = trans-membrane solvent flux ($ml/cm^2 \cdot sec$)

D_s = solute diffusion coefficient in the concentration boundary layer (cm^2/sec)

C_2 = solute concentration (g/cm^3)

X = coordinate perpendicular to the membrane surface (cm)
The concentration boundary layer extends from $X = 0$ at the interface with the bulk fluid phase to $X = \delta$ at the interface with the gel layer or membrane, as the case may be.

Boundary Condition (18b) expresses the equality of convective and diffusive solute transport at the boundary layer interface given the first of the assumptions stated prior to Eq. (18).

Eq. (18) is integrated once to yield

$$J_1 C_2 - D_s \frac{dC_2}{dX} = \text{Constant} \qquad (19)$$

which from Condition (18b) equals 0. The resulting first-order equation is in turn integrated, and Condition (18a) is invoked to yield

$$C_2(X) = C_b \cdot \exp(J_1 X / D_s) \qquad (20)$$

Finally, $X = \delta$ is substituted into Eq. (20), C_w is used to denote $C_2(\delta)$, a mass transfer coefficient k_s is defined as D_s/δ, and Eq. (20) with these substitutions made is solved for the flux J_1 to yield

$$J_1 = k_s \cdot \ln(C_w / C_b) \qquad (21)$$

Correlations of mass transfer coefficients (k_s) for diffusive flow of retained solutes away from the upstream membrane surface are available from the analogy between mass and heat transfer for various channel geometries with both turbulent (Calderbank and Moo-Young, 1961; Chilton and Colburn, 1934; Treybral, 1968) and laminar flow (Leveque, 1928) and Graetz solutions (Drew, 1931; Graetz, 1885, Jakob, 1949)).

As described previously, in the pre-gel-polarized region the solute concentration C_w at the membrane ($X = \delta$) is less than the threshold concentration C_g for gel layer formation, but high enough to provide a boundary layer with significant resistance to solvent transport. If the trans-membrane pressure drop ΔP and hence the convective flux J_1 increase, the concentration at the membrane C_w increases accordingly, until it reaches a value for which Eq. (21) is again satisfied.

Once C_w reaches a value of C_g, Eq. (21) becomes

$$J_1 = k_s \cdot \ln(C_g/C_b) \tag{22}$$

where k_s maintains its former value by virtue of the second assumption preceding Eq. (18). Now, however, the righthand side of Eq. (22) cannot adjust itself to compensate for an increased flux J_1. What happens instead is that an increase in ΔP produces an initial surge in the convective flux, which leads to an increased thickness of the gel layer. This in turn increases the resistance to solvent transport, and so reduces J_1 until finally it reaches its original value, at which point Eq. (22) is again satisfied.

The effect of an increase in the bulk solute concentration C_b on the flux is also predictable from the given relations. The model does not provide an explicit formula for the variation of the flux with C_b in the pre-gel-polarized region, where C_w is free to increase to satisfy Eq. (21). However, the flux (and hence the pressure drop) required to attain the gel-polarized state must be less for a higher bulk solute concentration, and consequently the J_1 vs. ΔP curve asymptotes to a lower value (given by Eq. (22)) at a lower pressure drop for a higher value of C_b, It might be expected that this behavior would be reflected by a decreasing flux with increasing C_b in the pre-gel region as well, a phenomenon which has in fact been observed (Blatt, Dravid, Michaels, and Nelsen, 1970).

Another postulate of the gel model is that as the concentration polarization modulus $M = C_w/C_b$ becomes significant, the solute rejection coefficient σ (in actuality σ_A but referred to as σ hereafter), defined as

$$\sigma = 1 - \frac{C_p}{C_b} \tag{23}$$

where C_p is the solute concentration in the permeate, is a function of both the membrane and boundary layer properties. (An obvious exception is the case of a membrane which is by itself impermeable to the solute.) In the pre-gel-polarized region, the concentration boundary layer contains rather mobile solute molecules which undergo relatively slight molecular interactions. As the concentration C_w at the membrane surface increases, it might be expected that solute would be carried through the pores at progressively higher rates. In consequence, if the pressure drop is increased for a given bulk solute concentration, C_w and therefore the modulus $M = C_w/C_b$ increase, and σ accordingly decreases (shown by Baker (1969) for dextran solutions); however, if C_b is increased for a given ΔP, C_w increases but the change in the modulus is uncertain, and consequently the variation of σ with C_b is indeterminate in the pre-gel-polarized region.

On the other hand, in the gel-polarized region the solute molecules adjacent to the membrane surface are largely immobile, and constitute an additional barrier to solute transport. The solute retention in this state should consequently be considerably greater than it was in the pre-gel-polarized region, and should also be relatively independent of the pressure drop and the bulk solute concentration, which in this case have no effect on conditions at the membrane surface.

The predicted dependences of the solvent flux and solute rejection on various system parameters may be summarized as follows:

(1) Flux (J_1) vs. pressure drop (ΔP). At low pressure drops (in the pre-gel-polarized region) J_1 increases with ΔP. Above some pressure drop (in the gel-polarized region) the solute concentration at the membrane surface reaches a value C_g, and thereafter J_1 remains at a constant value given by Eq. (22), regardless of further increases in ΔP.

(2) Flux (J_1) vs. bulk solute concentration (C_b). As C_b increases, the limiting (gel-polarized) value of J_1 given by Eq. (22) decreases, and occurs at a lower pressure drop. J_1 is also expected to decrease with increasing C_b in the pre-gel-polarized region, although this is not explicitly predicted by the model.

(3) Flux (J_1) vs. membrane solvent permeability ($\bar{P}_1$). As $\bar{P}_1$ increases, the flux J_1 has a higher value for a given pressure drop, and consequently (from Eq. (21)) C_w reaches C_g at a lower ΔP; J_1 thus reaches its pressure-independent asymptotic value (still given by Eq. (22)) at lower values of ΔP for membranes of increasing solvent permeability.

(4) Solute rejection (σ) vs. pressure drop (ΔP). At low pressure drops (corresponding to the pre-gel-polarized state) σ should decrease with increasing ΔP, and at higher pressure drops (corresponding to the gel-polarized state) σ should be independent of ΔP.

(5) Solute rejection (σ) vs. bulk solute concentration (C_b). The variation of σ with C_b is indeterminate at low pressure drops, and σ should be independent of C_b at higher pressure drops.

(2) Concentration Polarization Model for Microsolutes. Because of similar fluid dynamic and mass transfer factors controlling both macrosolute and microsolute polarization, the concentration polarization model for microsolute ultrafiltration is a simplified version of the gel model in which only one layer exists adjacent to the upstream membrane surface. This layer is the hydrodynamic concentration or polarization boundary layer of the pre-gel-polarized region. This region is identical to that found in reverse osmosis, which has been extensively investigated (references previously presented).

Resistances in Series Model for Overall Transport

Trans-membrane transport in an ultrafiltration system may be considered in terms of a series of hydraulic resistances including the membrane, the gel layer, and the concentration boundary layer for the most general case of the gel-polarized state (gel model). Blatt, et al. (1970) presented an analytical transport model based on their interpretation of the gel model.

Mathematical modeling of the gel-polarized region leads to the familiar relationship between the flux, the driving force, and a series of resistances, given by

$$J_1 = \frac{\Delta P}{R_m + R_g + R_p} \tag{24}$$

where

R_m = flux resistance of the membrane (psi·cm^2·sec/ml)

R_g = flux resistance of the gel layer (psi·cm^2·sec/ml)

R_p = flux resistance of the concentration boundary layer (psi·cm^2·sec/ml)

Realizing that Eqs. (1) and (24) should be identical when $R_g = 0$ and $R_p = 0$, R_m may be expressed as

$$R_m = \frac{t_m}{\bar{P}_1} \tag{25}$$

Similarly,

$$R_g = \frac{t_g}{\bar{P}_{1g}} \tag{26}$$

$$R_p = \frac{\delta}{\bar{P}_{1p}} \tag{27}$$

where

t_g = thickness of the gel layer (cm)

$\bar{P}_{1g}$ = gel-layer permeability constant for the solvent (ml/cm·sec·psi)

δ = thickness of the concentration boundary layer (cm)

$\bar{P}_{1p}$ = concentration-boundary-layer permeability constant for the solvent (ml/cm·sec·psi) $\bar{P}_{1p}$ is an average permeability since the solute concentration varies throughout this layer.

With $R_g = 0$ ($t_g = 0$), this model describes the pre-gel-polarized region including the membrane and the concentration boundary layer.

The solvent permeability of the gel layer is a complex function of the solute concentration and molecular characteristics. In some cases, $\bar{P}_{1g}$ for a solvent with unit viscosity may be approximated by the following Kozeny-Carman relation for porous solids (Blatt, Dravid, Michaels and Nelsen, 1970):

$$\bar{P}_{1g} = \frac{d^2}{180} \cdot \frac{\varepsilon^3}{(1 - \varepsilon)^2} \tag{28}$$

where

d = particle diameter (cm)

ε = porosity of the gel layer

$\bar{P}_{1g}$ has the units of (ml/cm·sec·psi)

In the pre-gel-polarized state the value of $\bar{P}_{1g}$ decreases as C_w increases, while in the gel-polarized state where $C_w = C_g$, $\bar{P}_{1g}$ remains constant.

The following two results may be predicted from this model:

(1) In the pre-gel-polarized state as ΔP increases, C_w increases with a resulting decrease in $\bar{P}_{1p}$. Therefore from Eqs. (24) and (27) with $R_g = 0$ and both R_m and δ constant, J_1 can be shown to increase less than proportionately with ΔP.

(2) The gel-polarized state is described by Eqs. (24) and (26) with R_m, R_p, and $\bar{P}_{1g}$ constant. J_1 is independent of ΔP since t_g adjusts to nullify changes in ΔP.

Elimination of Concentration Polarization

Trans-membrane flux reductions due to the concentration polarization effect can seriously restrict the usefulness of the ultrafiltration process. Therefore, a primary concern in ultrafiltration is the elimination or reduction of this flux-limiting phenomenon. Several approaches to this problem may be taken.

One approach involves process operation at flow and concentration conditions that maximize the rate of back diffusion from the upstream membrane surface (the controlling transfer step). Blatt, et al. (1970) reported that in laminar-flow systems operation at high flow velocities across membrane surfaces in thin, short channels maximizes the rate of back diffusion, while in turbulent-flow systems maximization is achieved by operating at high Reynolds numbers in thin channels with dilute solutions. Thomas and co-workers (Thomas, Griffith and Keller, 1971; Thomas and Kraus, 1964) studied the role of turbulence promoters in maximizing the wall shear rate and reducing concentration polarization. In another preventive approach specific feed pretreatment may be used to eliminate the solute-membrane interactions that cause the flux reductions.

Alternatively, certain feed additives and/or membrane cleaning techniques may be employed to remove fouling already present on the membrane surface. Mechanical removal methods include the following: (1) periodic depressurization; (2) high velocity water flushing; (3) flushing with a two-phase air-water mixture; and (4) direct oxmosis. In ultrafiltration of secondary effluent from an activated sludge plant, Weissman, Smith and Okey (1968) were able to restore the initial flux by mechanically removing the gel layer. Chemical methods may be used to clean the fouled membrane surface, but this cleaning must not damage the flux or rejection characteristics of the membrane. Enzymes and/or sodium perborate are possible chemical additives. Nusbaum, Cruver and Sleigh (1972) found the enzyme detergent Biz^R (manufactured by the Procter and Gamble Company), ethylenediaminetetraacetic acid (EDTA), and sodium perborate to be about equally effective in removing membrane fouling. In systems using this type of

cleaning periodically the average flux decline was much lower than in systems operated similarly but with no cleaning. It is quite possible that Biz was effective not as a consequence of its enzyme content but as a consequence of oxidative reactions between sodium perborate (a principle component of Biz) and the gel material.

SECTION IV

OBJECTIVES

The objective during the first year of the grant-supported research was to design, construct, and implement a high-pressure, dynamic flow-through ultrafiltration test loop to permit evaluation of a variety of membranes and a variety of feed solutions simulating sewage treatment or pollution abatement via ultrafiltration. The purpose of the second and third year program was to determine the contribution to flux-limiting concentration polarization by specific solute-membrane interactions as opposed to nonspecific material balance factors.

Apparently, the major limitation of ultrafiltration as a viable means of waste water reclamation is concentration polarization or the deposition on the membrane of a diffusion-limiting gel layer. This polarization can be minimized in theory by judicious design of the feed flow pattern across the membrane; however, to do so could require rather costly capital expenditures and large energy inputs to minimize the boundary layer thickness. Another factor which contributes to solute-polarization is the molecular structure of the solute itself. The present studies are intended to reveal those molecular features (functional groups, asymmetry, polarity, ionic nature) which affect concentration polarization. A possible application of this study might be the determination that one component of a multicomponent solute feed may particularly contribute to polarization. Recognition of this phenomenon would suggest selective pretreatment of the feed to remove the hyper-polarizing substance.

A polyelectrolyte complex membrane, characterized by a slight nonstoichiometric excess of polyanion, and a nonionic, asymmetric cellulose acetate membrane were used in conjunction with a nonionic surfactant (polyoxyethyleneoctylphenol (Triton X-100^{R})), an anionic surfactant (sodium dodecylbenzenesulfonate), and a nonsurfactant (polyethylene glycol (Carbowax 600^{R})). Carbowax 600, a symmetrical molecular analog of Triton X-100, is not surface-active but is similar in virtually all other physicochemical properties. As a consequence, the differences between the effects of Carbowax 600 and Triton X-100 on the trans-membrane flux served to characterize the contribution of molecular asymmetry and therefore surface activity to flux-limiting solute-membrane interactions. An investigation of trans-membrane fluxes associated with the ultrafiltration of anionic surfactant solutions helped to determine the influence of solute ionic charge on flux-limiting behavior of both a neutral and a charged membrane. The results of these studies were used to correlate observed flux-limiting and solute rejection effects with the membrane type and the surface-active properties of the solute. In addition, the trans-membrane flux and solute rejection results obtained by varying the trans-membrane pressure drop and the upstream bulk solute concentration were used to determine the validity of existing concentration polarization models.

As previously indicated, the trans-membrane flux may be described in terms of a series of hydraulic resistances including the membrane, the gel layer, and the concentration boundary layer for the most general case of the gel-polarized state in the gel model. This result can most clearly be shown by Eq. 24;

$$J_1 = \frac{\Delta P}{R_m + R_g + R_p} \tag{24}$$

To account for the flux resistance due to the specific solute-membrane interactions, an additional resistance term can be incorporated into the series of resistances modifying Eq. 24 to yield

$$J_1 = \frac{\Delta P}{R_m + R_g + R_p + R_i} \tag{29}$$

where

R_i = flux resistance due to specific solute-membrane interactions ($psi \cdot cm^2 \cdot sec/mol$)

Since in this study the flux resistances of both the gel layer (R_g) and the concentration boundary layer (R_p) as determined from the Carbowax 600 data were either negligible or measurable, then any further flux reductions from the pure distilled water level due to the addition of surfactant can be attributed to the flux resistance of the specific solute-membrane interactions (R_i).

SECTION V

EXPERIMENTAL DESIGN

Apparatus

A six-cell test loop was constructed complete with instrumentation to maintain the upstream pressure, flow rate of the upstream solution, trans-membrane flux rate, permeate quality, and temperature of the upstream solution. The front and rear views of the completed unit are shown in Figures 1 and 2. Stainless steel Millipore high pressure filter cells with thin channels are positioned along two parallel manifolds with three cells on each manifold. The solutions under test are recycled through each flow loop by a duplex MilRoyal control volume diaphragm pump. This arrangement permits simultaneous operation at two different pressures. Stainless steel (316) valves, fittings, and tubing are arranged such that the three cells in each manifold can be operated in series or parallel. Also any cell can be eliminated from the flow loop without affecting the operation of the remaining cells. Each manifold in the system includes an accumulator and a back pressure regulator (balanced by a high pressure nitrogen cylinder) to eliminate flow rate fluctuations and to allow operation at an elevated, steady pressure. A micrometer valve positioned between the last cell and the reservoir of each manifold allows precise control of the upstream solution flow rate. Each cell contains an upstream pressure gauge, and a rotameter between the micrometer valve and the reservoir is used to determine the upstream solution flow rate. The temperature of the upstream solution in each manifold is regulated by passing the solution through a tubular heat exchanger in series with a temperature controlled water bath prior to delivery to the ultrafiltration cells. The system is capable of constant temperature operation at controlled pressures up to 2175 psi and upstream solution flow rates up to 14.4 gph (gallons/hour) per side of the pump.

The experimental set-up used in this study of the effect of solute asymmetry on concentration polarization is shown in Figure 3. The solution under test is recycled through the flow loop with the three ultrafiltration cells of each manifold connected in series. Because of the negligible pressure drop and concentration change between cells, this series operation of the cells provides three replicate results for every test. The upstream solution is recycled through a five gallon reservoir.

A circular membrane with an exposed surface area of 9.6 cm^2 is used in each ultratiltration cell. The channel height, or the clearance between the membrane surface and the cell surface, is approximately 55 mils.

Fig. 1. Front view of the ultrafiltration test loop

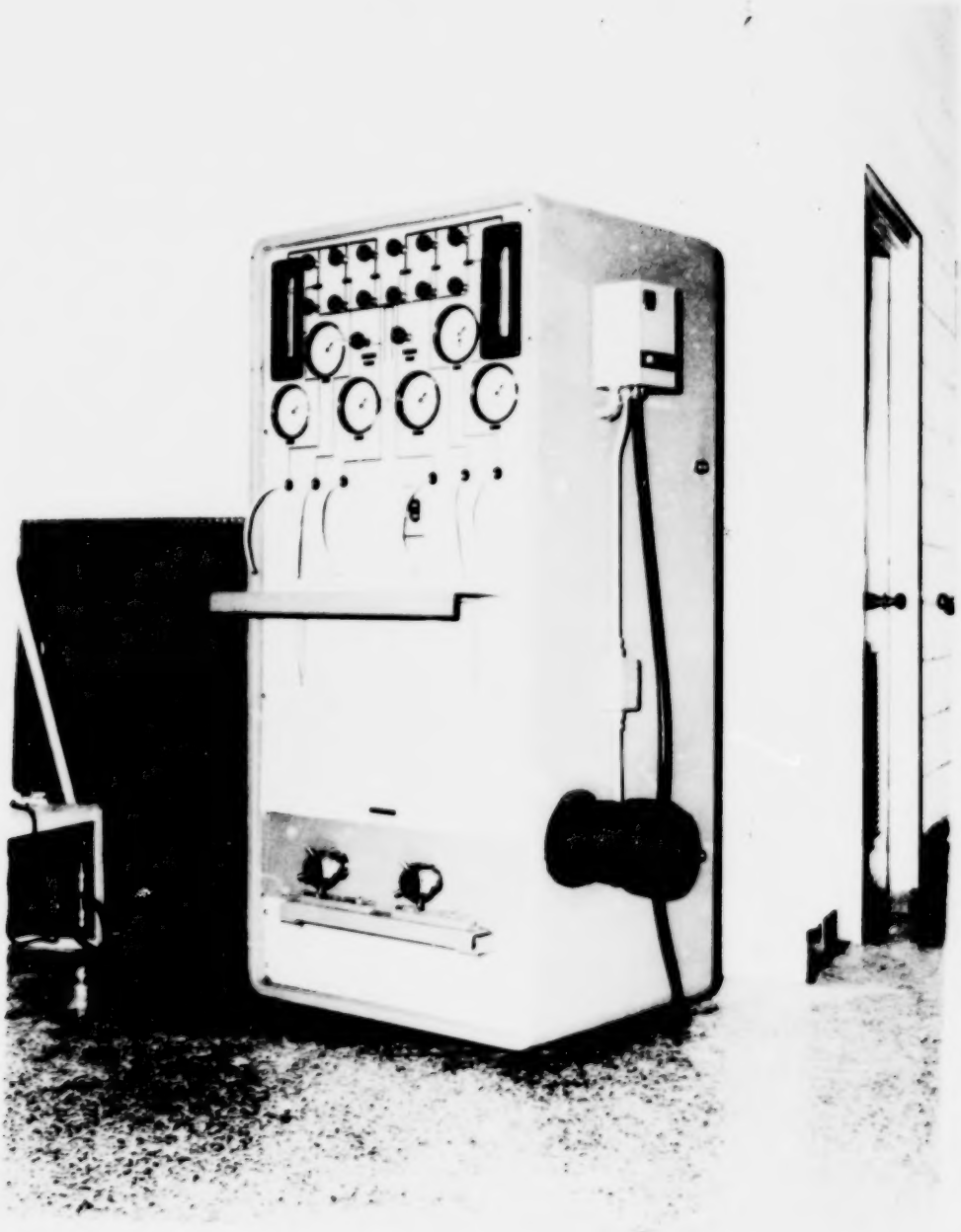


Fig. 2. Rear view of the ultrafiltration test loop

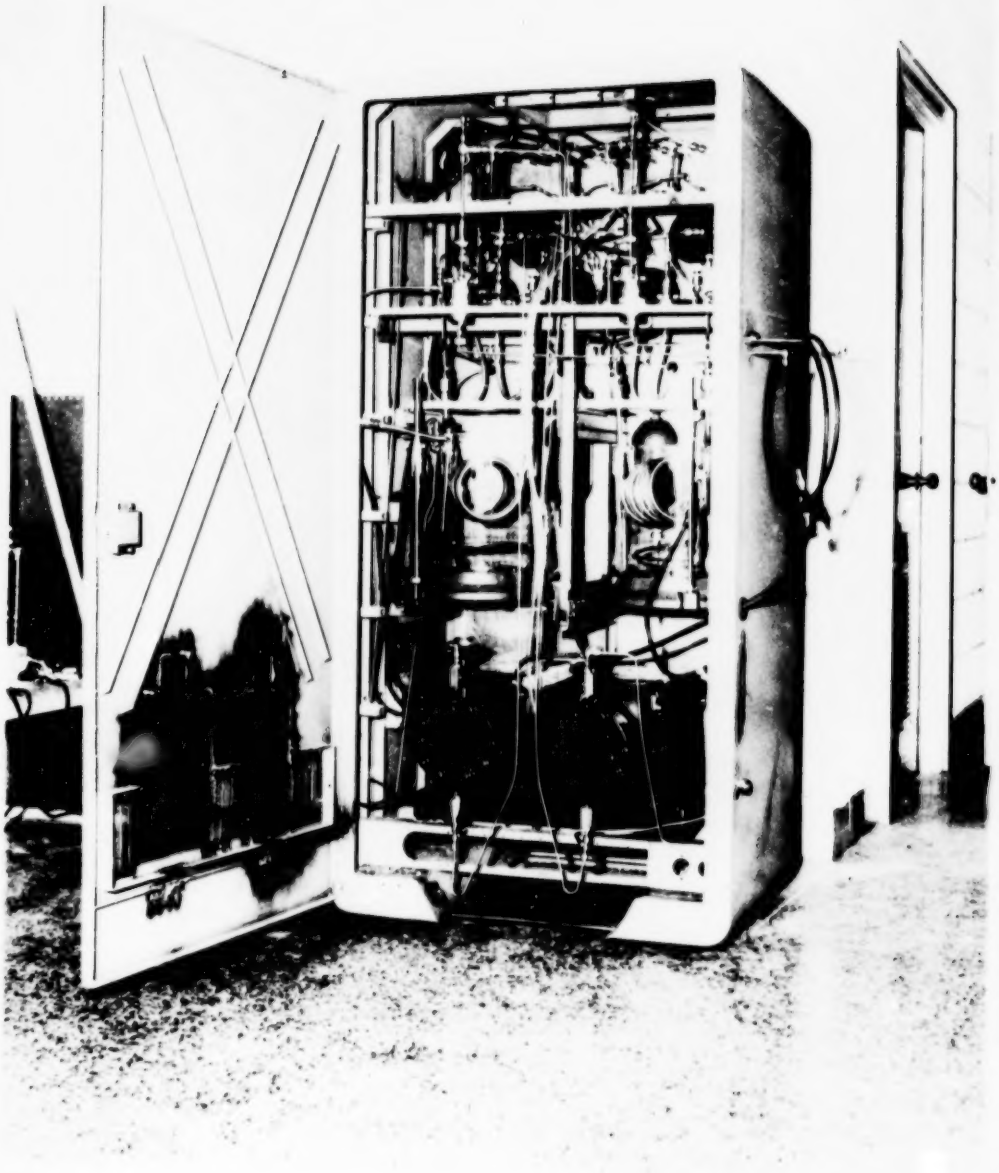
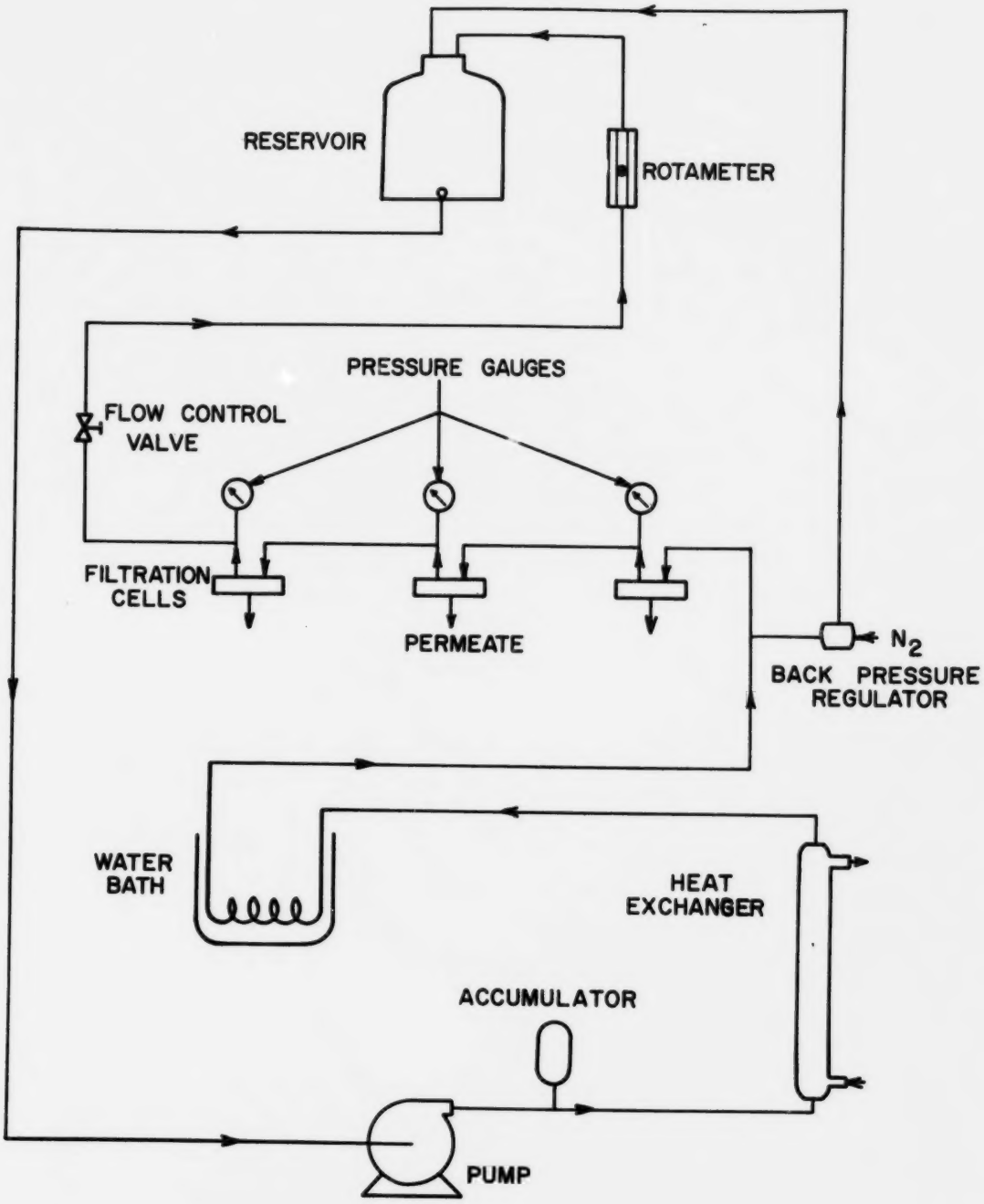


Fig. 3. Flow diagram for the ultrafiltration apparatus


RESERVOIR
ROTAMETER
PRESSURE GAUGES
FLOW CONTROL VALVE
FILTRATION CELLS
PERMEATE
N_2
BACK PRESSURE REGULATOR
WATER BATH
HEAT EXCHANGER
ACCUMULATOR
PUMP

The fluid impinges on the center of the membrane and spreads radially to the outer membrane edge where it is collected for delivery to other parts of the system. For the constant flow rate maintained in this study of 27.5 ml/min (0.436 gallons/hour) across the membrane surface, the radial flow velocity decreases from about 0.1 ft/sec at the membrane center to about 0.01 ft/sec at the outer membrane edge.

Membranes

A polyelectrolyte complex membrane, characterized by a slight non-stoichiometric excess of polyanion, and a nonionic, asymmetric cellulose acetate membrane were used in this study. The polysalt membrane, designated UM-05^{R}, is commercially available from the Amicon Corporation. Specifications for this membrane predict rejection of molecules with molecular weights greater than approximately 500. The cellulose acetate membrane is supplied for commercial use by the Tennessee Eastman Corporation and is designated KP-90^{R}.

Solutes

Two of the solutes studied can be characterized as surfactants possessing a hydrophilic end and hydrophobic end. Triton X-100^{R} (Rohm and Hass trade name for polyoxyethyleneoctylphenol (N=0)) is a nonionic surfactant with an average molecular weight of approximately 625. Sodium dodecylbenzenesulfonate is an anionic surfactant, with an anionic molecular weight of approximately 325. This surfactant was prepared by neutralization of dodecylbenzenesulfonic acid with sodium hydroxide. The third solute is a symmetrical nonsurfactant, Carbowax 600^{R} (Union Carbide trade name for polyethylene glycol) which has an average molecular weight of approximately 600.

Transport Measurements

Data were collected for each of the two membranes with pure distilled water and each solute at two concentrations for three trans-membrane pressure drops. Solute concentrations of 100 ppm (parts per million by weight) and 1000 ppm were chosen to show the influence of trace amounts of surfactant. For the cellulose acetate membrane hydraulic pressure drops across the membrane of 290 psi, 200 psi, and 100 psi were tested; for the polysalt membrane the pressure drops tested were 100 psi, 70 psi, and 40 psi. For both membranes these trans-membrane pressure ranges corresponded to a flux range of about 5 to 20 gfd (gallons/day·ft^{2}). The osmotic pressure difference for the 1000 ppm

sodium dodecylbenzenesulfonate solution was approximately 1.0 psi; therefore, osmotic pressure differences for the three solutes at the concentrations investigated could be neglected.

A constant upstream solution flow rate over the membrane surface of approximately 1000 gfd was maintained. In all cases studied, the percentage recovery, or the ratio of the permeate flow rate to the upstream solution feed rate, was less than 2.5%. For these permeation rates and the ultrafiltration times used in this study, the upstream solution concentration could be considered constant. The temperature bath was controlled so that the upstream solution temperature in the ultrafiltration cells remained constant at 28°C.

The trans-membrane flux was determined volumetrically. Permeate delivered directly from the ultrafiltration cell by gravity was collected in a graduated cylinder for time intervals of both long (300 to 1000 minutes) and short (5 to 15 minutes) duration. The time dependences of the flux and solute rejection were determined for each membrane-solute combination, and the values corresponding to an ultrafiltration time of about 1700 minutes, by which time a constant flux was invariably achieved, were correlated with the trans-membrane pressure drop and solute concentration.

When possible, for each solute a single membrane set was subjected to all of the experimental conditions. After each test at a given set of conditions, the system with the membranes in place was rinsed for at least 12 hours with distilled water and subjected to further testing to give an indication of the permanence of the solute-induced flux-limiting effects.

The series operation of the cells provided an indication of the precision of the results. For the sake of brevity results for only one of the cells are presented. While the absolute values obtained for the other cells differed from those shown, presumably due to variations between membranes of the same composition, the magnitudes of the observed flux reduction and solute retention effects were closely duplicated in each cell.

Analytical Determination of Solute Concentrations

Triton X-100 concentrations were determined by ultraviolet spectrophotometry, using a Beckman Grating Spectrophotometer (model DB-GT) at a wavelength of 277 nanometers. Sodium dodecylbenzenesulfonate concentrations were determined from solution conductivity measurements, using a Radiometer conductivity meter (Type CDM2e No. 111255) and conductivity cell (Type CDC 114). Carbowax 600 concentrations were determined by a simple but extremely accurate analytical procedure, using a reagent solution (prepared from bismuth subnitrate, potassium iodide, glacial acetic acid, and barium chloride) to form a colloidal complex with the

Carbowax 600. This complex may be centrifuged in a Goetz cell, and the precipitate volume correlated with the Carbowax 600 concentration. This exact procedure is the proprietory knowledge of the Chemstrand Corporation.

SECTION VI

RESULTS AND DISCUSSION

Flux Reduction Due to Membrane Compaction

Flux versus time relations for pure distilled water passing through both the cellulose acetate membrane and the polysalt membrane are presented in Figure 4. The results shown for each membrane correspond to a particular pressure drop, but are representative of the results obtained for all pressure drops used in the study. As the figure indicates, after several minutes there was no apparent flux decline associated with compaction for either membrane.

Results for a Specific Solute-Membrane Combination

In Figures 5 and 6 the trans-membrane flux and solute rejection for Triton X-100 and the cellulose acetate membrane are shown. In all cases there was a significant flux reduction associated with the presence of the nonionic surfactant in the feed. The greatest portion of the flux decline can be attributed to the addition of the first 100 ppm of Triton X-100, for which the decline varied from 13% at ΔP = 100 psi to 17% at 290 psi. At 1000 ppm, the flux reduction associated with the cellulose acetate membrane was essentially independent of pressure drop, remaining constant at about 25%.

For both solute concentrations there was an increase followed by a decrease in solute retention as the pressure drop increased, and for a given pressure drop the retention noticeably increased as the concentration increased from 100 ppm to 1000 ppm. The increased rejection obtained with the 1000 ppm feed may be a consequence of exceeding the critical micelle concentration of Triton X-100, which has been estimated to be approximately 100 ppm using data of Fowkes (1953). Micellar material is more effective in forming the gel-like barrier at the upstream membrane surface, and in addition the micelles would probably be totally rejected by the membrane, resulting in a much higher apparent rejection of surface-active solute.

The degree of permanence of the observed surfactant-induced flux reduction was studied by flushing the entire system with the membrane in place for approximately 12 hours with distilled water, and comparing the resulting pure solvent flux with that measured prior to ultrafiltration. The results are summarized in Table 1. It was found that at the conclusion of the rinse the fluxes returned to approximately their original levels in all but two cases -- ΔP = 200 psi and ΔP = 290 psi for the 1000 ppm solution. As Table 1 also shows, the irreversible flux reduction for these two cases is identical to the reduction obtained in going

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Fig. 4. Time dependence of the trans-membrane flux

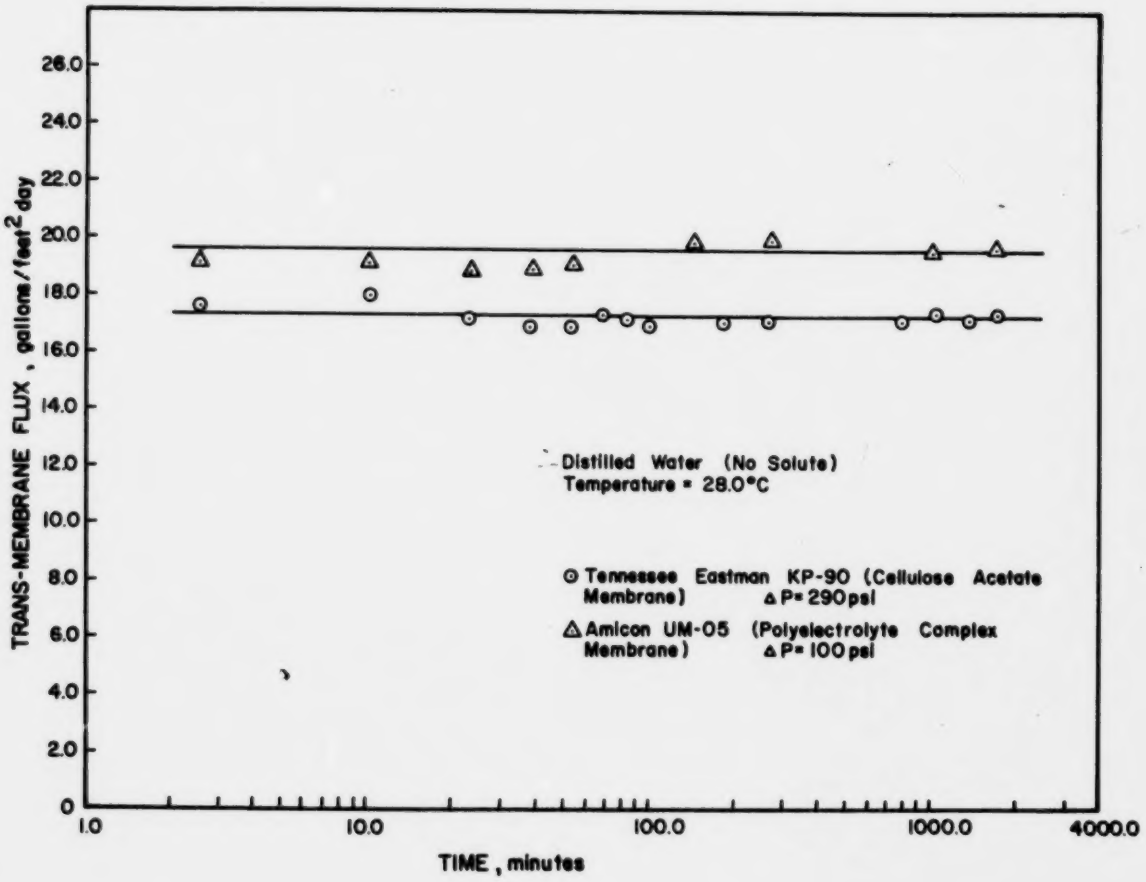

TRANS-MEMBRANE FLUX , gallons/feet^2 day
26.0
24.0
22.0
20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0
1.0
10.0
100.0
1000.0
4000.0
TIME , minutes
Distilled Water (No Solute)
Temperature = 28.0°C
⊙ Tennessee Eastman KP-90 (Cellulose Acetate Membrane) ΔP= 290psi
△ Amicon UM-05 (Polyelectrolyte Complex Membrane) ΔP= 100 psi

Fig. 5. Effect of Triton X-100 concentration on the trans-membrane flux through a cellulose acetate membrane

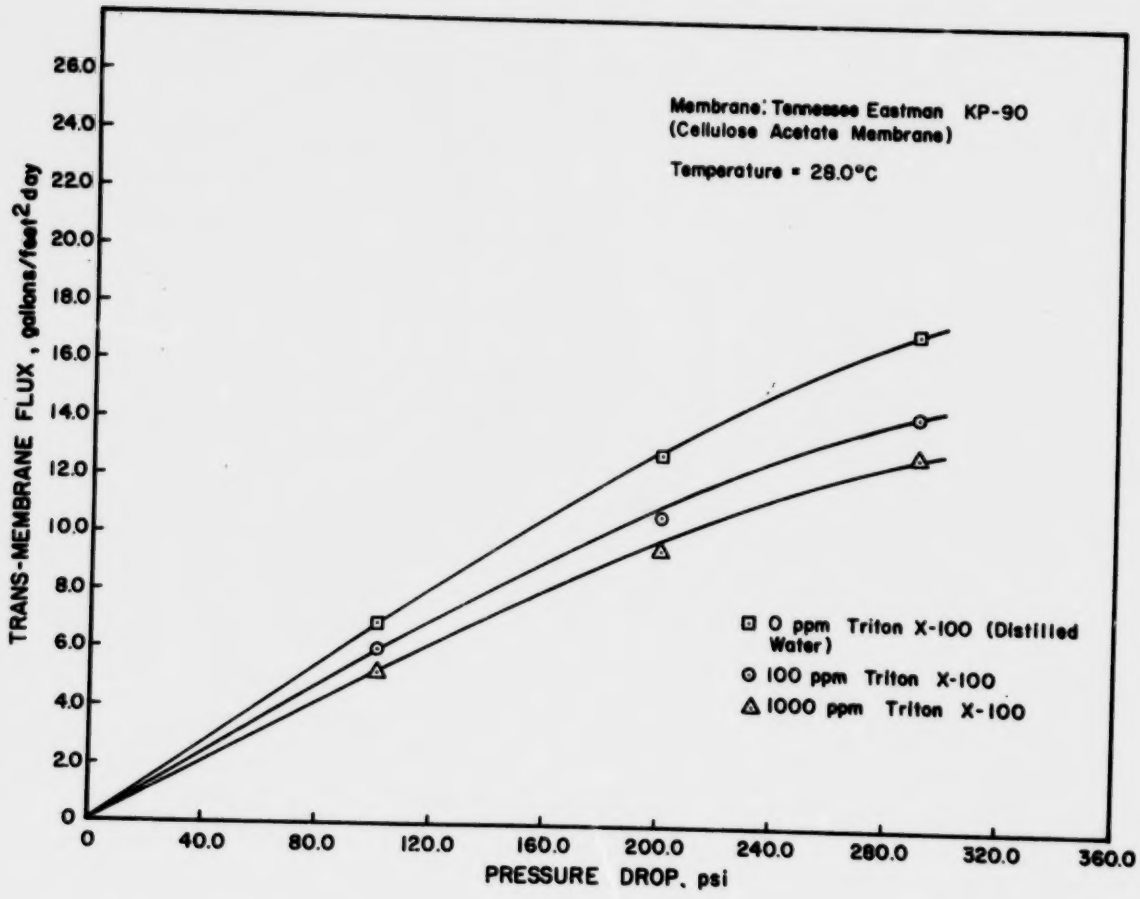

Membrane: Tennessee Eastman KP-90
(Cellulose Acetate Membrane)
Temperature = 28.0°C
TRANS-MEMBRANE FLUX, gallons/feet² day
PRESSURE DROP, psi
0 ppm Triton X-100 (Distilled Water)
100 ppm Triton X-100
1000 ppm Triton X-100
0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
22.0
24.0
26.0
0
40.0
80.0
120.0
160.0
200.0
240.0
280.0
320.0
360.0

Fig. 6. Effect of Triton X-100 concentration on the solute rejection by a cellulose acetate membrane

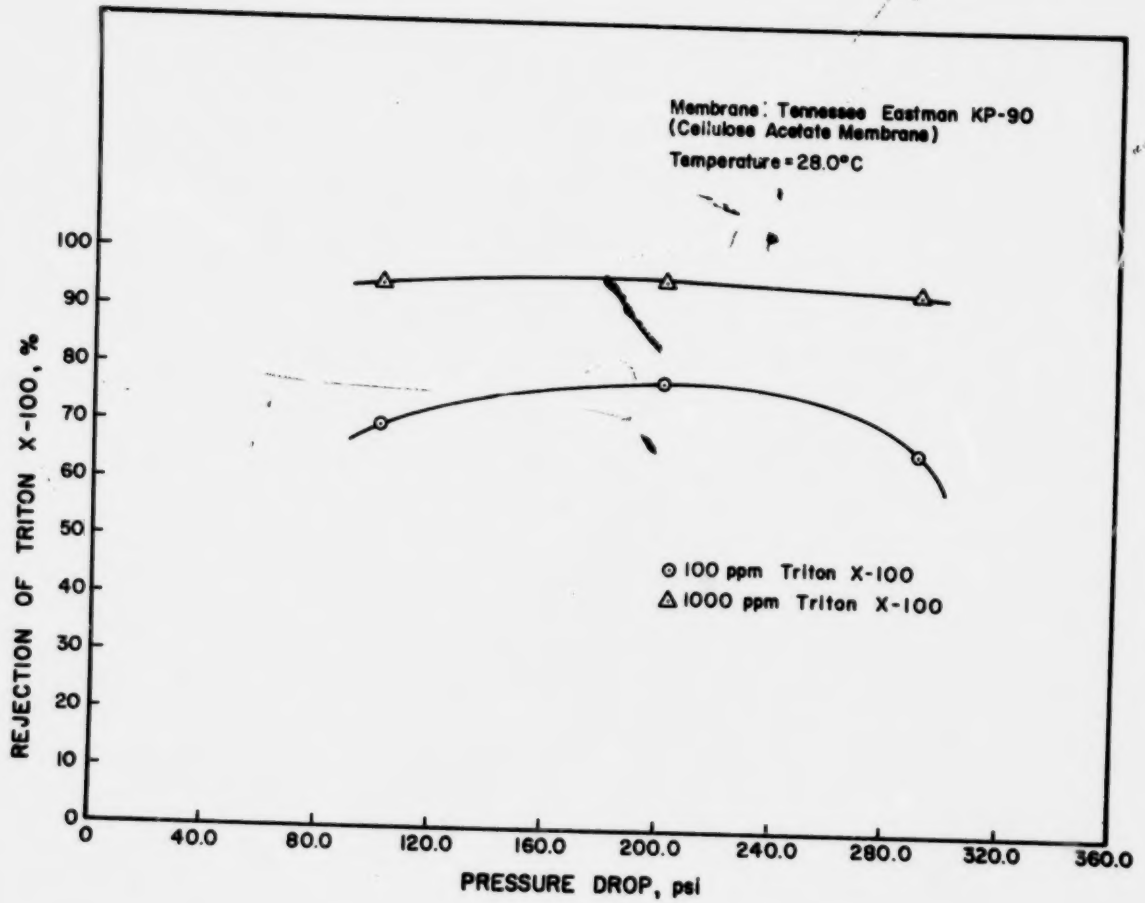

Membrane: Tennessee Eastman KP-90
(Cellulose Acetate Membrane)
Temperature = 28.0°C
⊙ 100 ppm Triton X-100
△ 1000 ppm Triton X-100
REJECTION OF TRITON X-100, %
PRESSURE DROP, psi
0
10
20
30
40
50
60
70
80
90
100
0
40.0
80.0
120.0
160.0
200.0
240.0
280.0
320.0
360.0

Table 1. Reversibility of the Triton X-100-Cellulose Acetate Membrane Interactions*

Trans-Membrane Pressure Drop psi	Trans-Membrane Flux gallons/day-feet^2			
	0 ppm Triton X-100	100 ppm Triton X-100	1000 ppm Triton X-100	Distilled Water Rinse after 1000 ppm Triton X-100 Fouling
100	6.9	6.0	5.2	6.9
200	12.9	10.8	9.6	11.7
290	17.3	14.4	13.0	15.9

*Results obtained for a single cellulose acetate membrane.

from the 100 ppm to the 1000 ppm solution. The data, although consistent, are insufficient to provide an unequivocal conclusion concerning the nature of the irreversibility.

Results analogous to those given above were obtained for the other surfactant-membrane combinations, and are shown in Figures 7 through 12. The sections that follow deal separately with the results pertaining to flux reduction and solute retention of surfactant solutions.

Results for Flux Reduction of Surfactant Solutions

In most cases there was a noticeable reduction in the ultrafiltration flux associated with the presence of a surfactant in the feed. The fluxes for both membranes dropped as the bulk solute concentration of either surfactant increased, and either increased or remained constant as the trans-membrane pressure drop increased. These re , are consistent with the predictions of the gel model (Blatt, Dravid, Michaels, and Nelsen, 1970). The maximum flux reductions for all surfactant-membrane combinations studied are summarized in Table 2.

The most significant flux reduction -- that found for the nonionic surfactant (Triton X-100) and the cellulose acetate membrane -- ranged from 13% to 17% at 100 ppm to a maximum value of 25% at 1000 ppm. The curves for flux versus pressure drop were concave toward the pressure axis, but the flux never reached a constant value, suggesting that the system was in a pre-gel-polarized state for all pressure drops investigated.

For the Triton X-100-polysalt membrane combination, both the 100 ppm and the 1000 ppm solutions caused a flux reduction of 8% to 11%, except for the 1000 ppm solution at a ΔP of 100 psi, for which the reduction was about 24%. Somewhere above a pressure drop of 70 psi, the flux for the 1000 ppm solution appeared to level off with increasing ΔP, as would be expected if the system were in the gel-polarized state.

A considerable flux reduction was also observed for the polysalt membrane-sodium dodecylbenzenesulfonate (SDBS) combination at a solute concentration of 100 ppm. The shapes of the curves for flux vs. ΔP are again suggestive of the pre-gel-polarized state. The 20% flux decline at ΔP = 100 psi following the addition of 100 ppm of SDBS was only slightly below that found for 1000 ppm of Triton X-100 with the same type of membrane.

When the polysalt membrane was used to ultrafilter a 1000 ppm solution of SDBS, the flux increased rapidly to an anomalously high value, while the solute retention dropped to almost 0. At the conclusion of the ultrafiltration, the membrane was found to have been converted into an amorphous soap-like mass, suggesting that by some ion exchange mechanism

Table 2. Maximum Flux Reduction

Membrane and Pressure Drop		Solute: Triton X-100 100 ppm	Triton X-100 1000 ppm	SDBS 100 ppm	SDBS 1000 ppm
	Cellulose Acetate 290 psi	17%	25%	7%	10%
	Polysalt 100 psi	11%	24%	20%	*

*Membrane destroyed by test conditions.

Fig. 7. Effect of Triton X-100 concentration on the trans-membrane flux through a polysalt membrane.

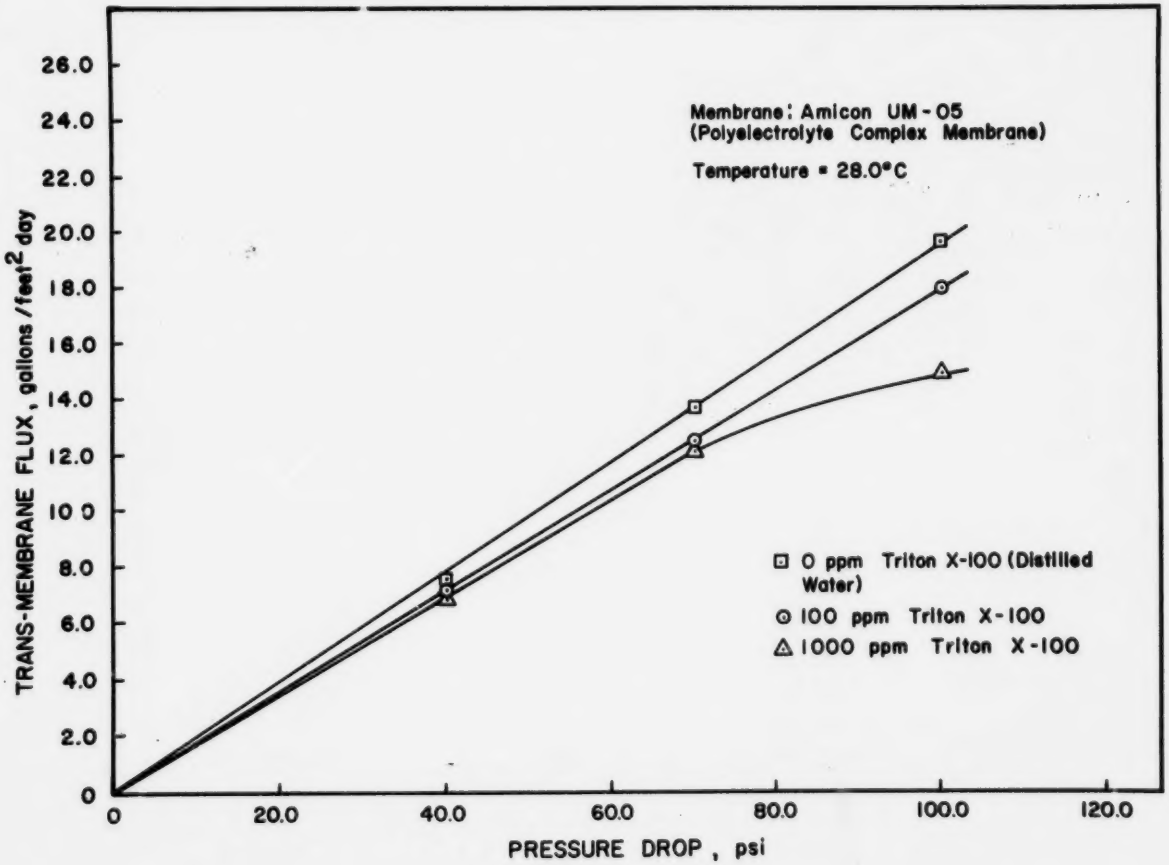
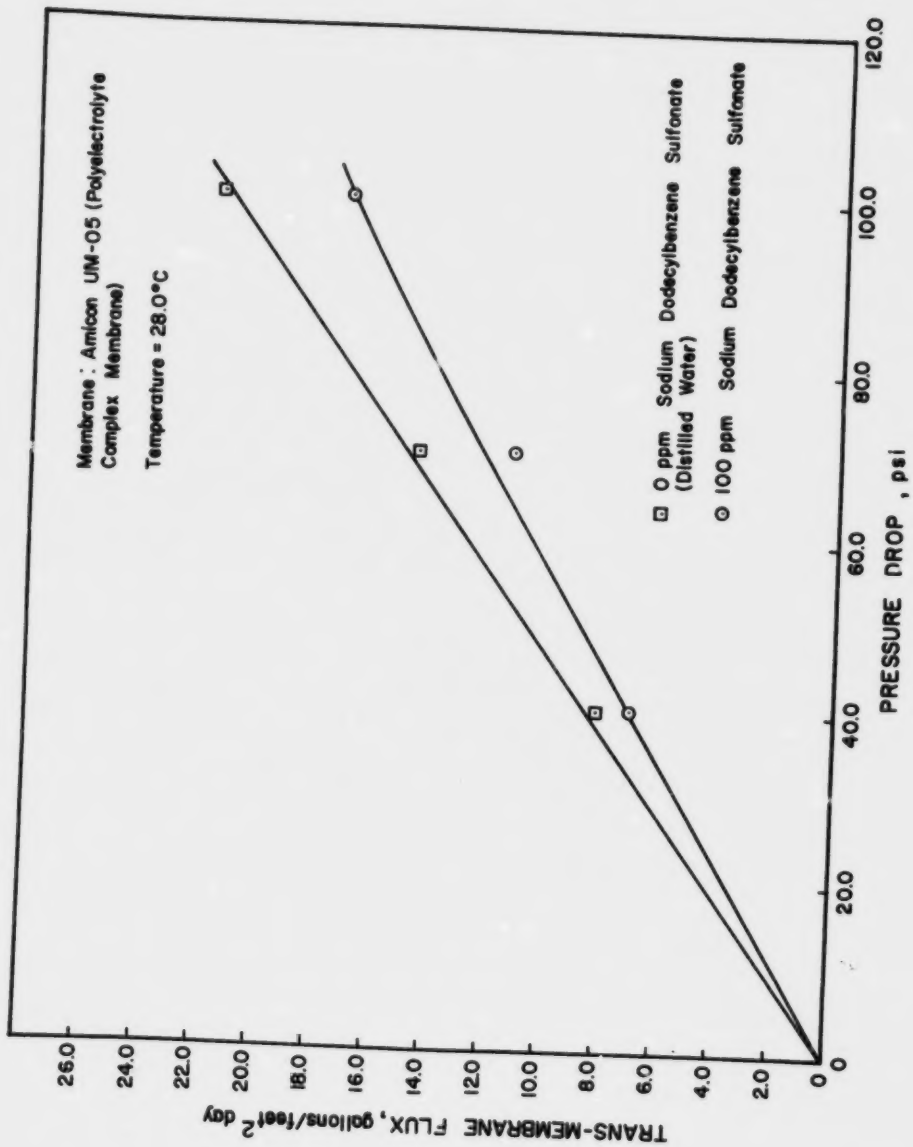

Membrane: Amicon UM-05
(Polyelectrolyte Complex Membrane)
Temperature = 28.0°C
□ 0 ppm Triton X-100 (Distilled Water)
⊙ 100 ppm Triton X-100
△ 1000 ppm Triton X-100
TRANS-MEMBRANE FLUX, gallons/feet² day
PRESSURE DROP, psi
0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
22.0
24.0
26.0
0
20.0
40.0
60.0
80.0
100.0
120.0

Fig. 8. Effect of sodium dodecylbenzenesulfonate concentration on the trans-membrane flux through a polysalt membrane


Membrane : Amicon UM-05 (Polyelectrolyte Complex Membrane)
Temperature = 28.0°C
□ 0 ppm Sodium Dodecylbenzene Sulfonate (Distilled Water)
○ 100 ppm Sodium Dodecylbenzene Sulfonate
TRANS-MEMBRANE FLUX, gallons/feet² day
PRESSURE DROP , psi
0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
22.0
24.0
26.0
0
20.0
40.0
60.0
80.0
100.0
120.0

the dodecylbenzenesulfonate radical had replaced the anionic component of the membrane. This behavior presumably is the reason for the well-known unsuitability of polysalt membranes for use with strongly ionic surfactants and detergents.

The flux-limiting effect of SDBS on the cellulose acetate membrane was the smallest observed for any surfactant-membrane combination. The percentage reductions shown in Table 2 give a somewhat exaggerated impression of this effect, since the flux at the pressure drop cited (ΔP = 100 psi) was relatively low to begin with. At higher pressure drops and correspondingly higher fluxes, the percentage reductions for this combination were of the order of 2 to 4%.

As noted previously the observed flux reductions were found to be reversible to a distilled water rinse, with the exception of that for the 1000 ppm Triton X-100-cellulose acetate membrane combination. In addition, duplicate tests with the same membranes used for the original runs were performed at random to provide another indication of the permanence of the solute-membrane interactions. For all of these tests except again those with Triton X-100 and the cellulose acetate membrane, the measured fluxes were within 1% of their values in the first set of runs. The irreversible nature of the Triton X-100-cellulose acetate membrane fouling caused a flux deviation of as much as 6.5% for 100 ppm Triton X-100 at ΔP = 200 psi. In all of the duplicate tests, both the fluxes and solute retentions were slightly depressed from their original values.

Results for Solute Retention of Surfactant Solutions

In most cases, there was little or no change in solute retention as the surfactant concentration or the trans-membrane pressure drop increased. The exceptions were observed for the 100 ppm Triton X-100-cellulose acetate membrane combination, for which an increase followed by a decrease in solute retention with increasing ΔP was observed, and the 100 ppm Triton X-100-polysalt membrane combination, for which an apparently considerable increase in σ was observed with increasing ΔP. The retention was relatively constant when SDBS solutions were ultrafiltered, except for the 1000 ppm solution-polysalt membrane combination, for which the membrane was destroyed.

The observed tendency of the solute retention to increase with an increasing trans-membrane pressure drop is opposite to the result obtained by Baker (1969) for the ultrafiltration of dextran solutions, and contradicts the prediction of the gel model as formulated by Blatt *et al.* (1970). Several explanations of this apparent contradiction might be postulated without departing from the basic descriptive framework of the model. In all probability, the expected increase in solute retention characteristic of the transition from the pre-gel to the gel-

Fig. 9. Effect of sodium dodecylbenzenesulfonate concentration on the trans-membrane flux through a cellulose acetate membrane

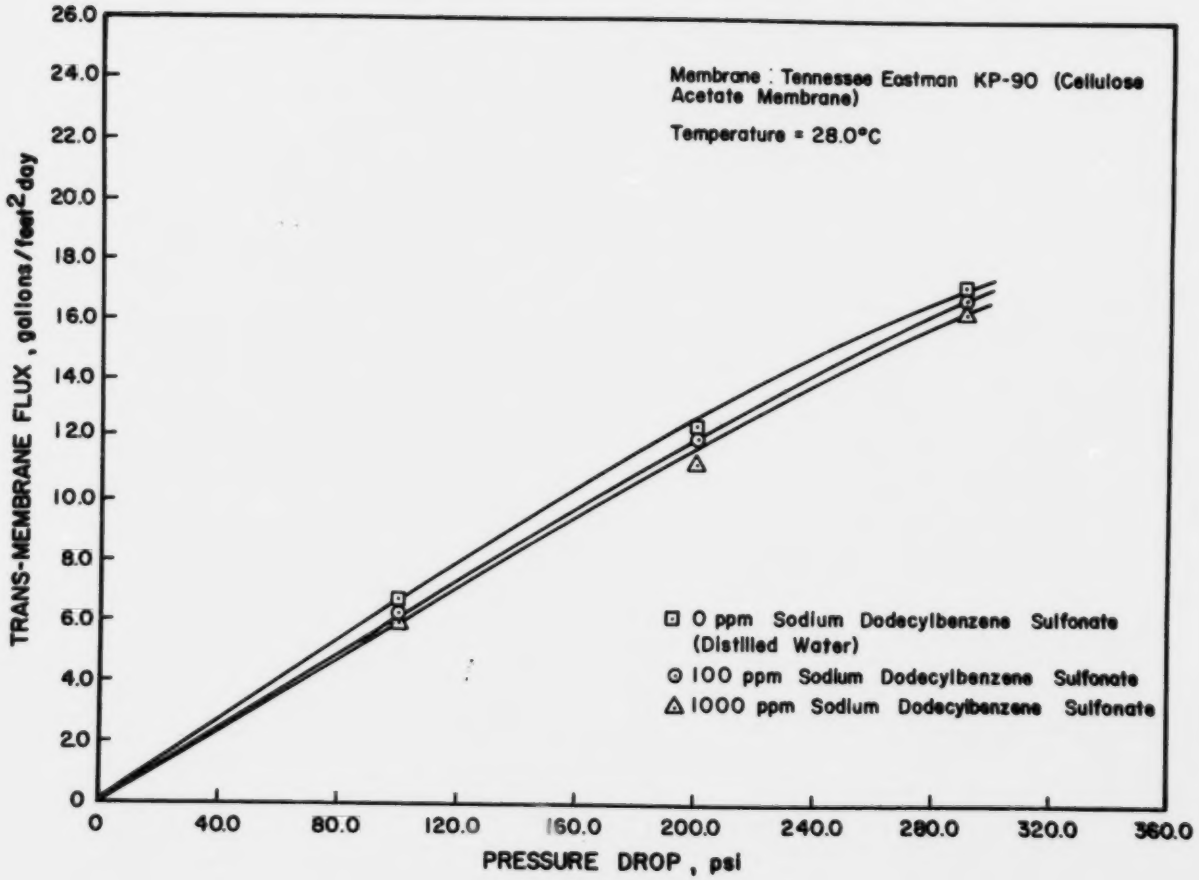

Membrane : Tennessee Eastman KP-90 (Cellulose Acetate Membrane)
Temperature = 28.0°C
□ 0 ppm Sodium Dodecylbenzene Sulfonate (Distilled Water)
○ 100 ppm Sodium Dodecylbenzene Sulfonate
△ 1000 ppm Sodium Dodecylbenzene Sulfonate
TRANS-MEMBRANE FLUX , gallons/feet^{2}day
PRESSURE DROP , psi
0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
22.0
24.0
26.0
0
40.0
80.0
120.0
160.0
200.0
240.0
280.0
320.0
360.0

Fig. 10. Effect of Triton X-100 concentration on the solute rejection by a polysalt membrane

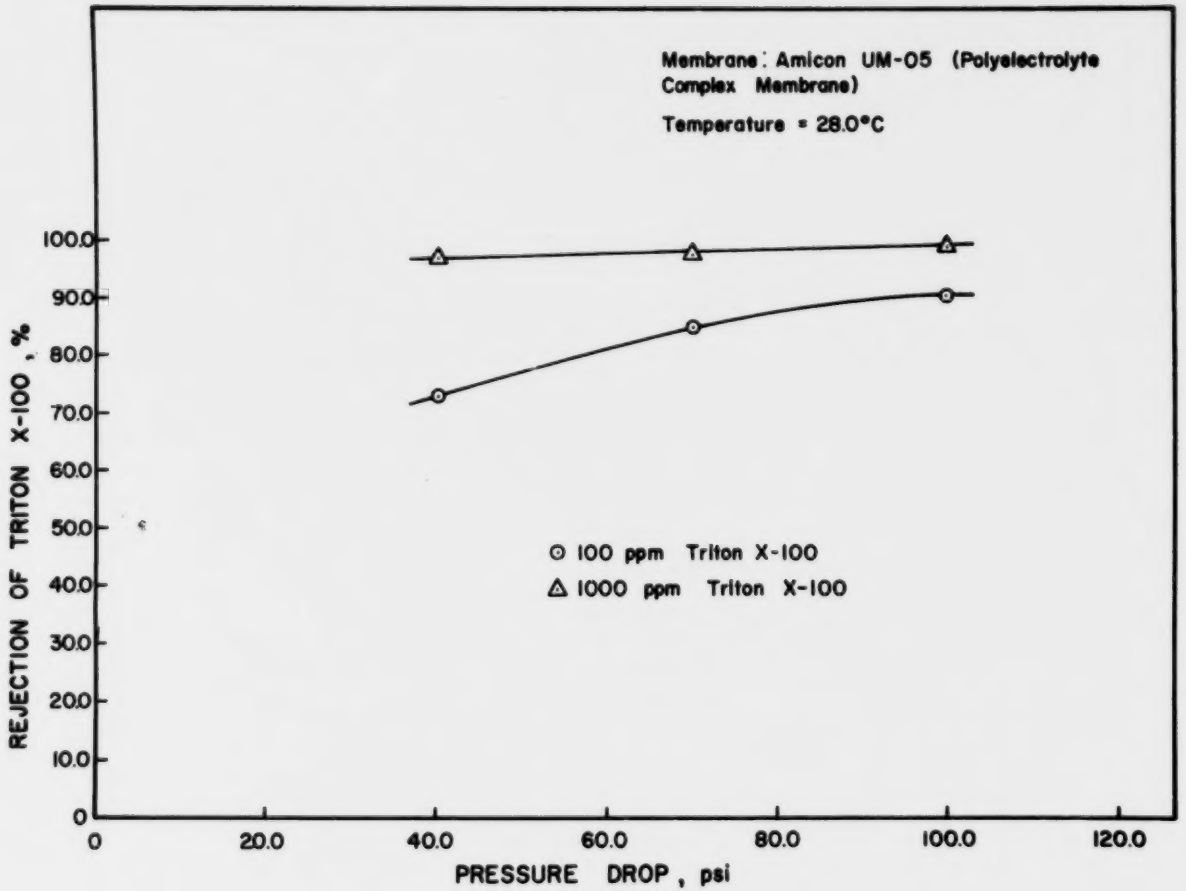

Membrane: Amicon UM-05 (Polyelectrolyte Complex Membrane)
Temperature = 28.0°C
REJECTION OF TRITON X-100, %
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
0
20.0
40.0
60.0
80.0
100.0
120.0
PRESSURE DROP, psi
⊙ 100 ppm Triton X-100
△ 1000 ppm Triton X-100

Fig. 11. Effect of sodium dodecylbenzenesulfonate on the solute rejection by a polysalt membrane

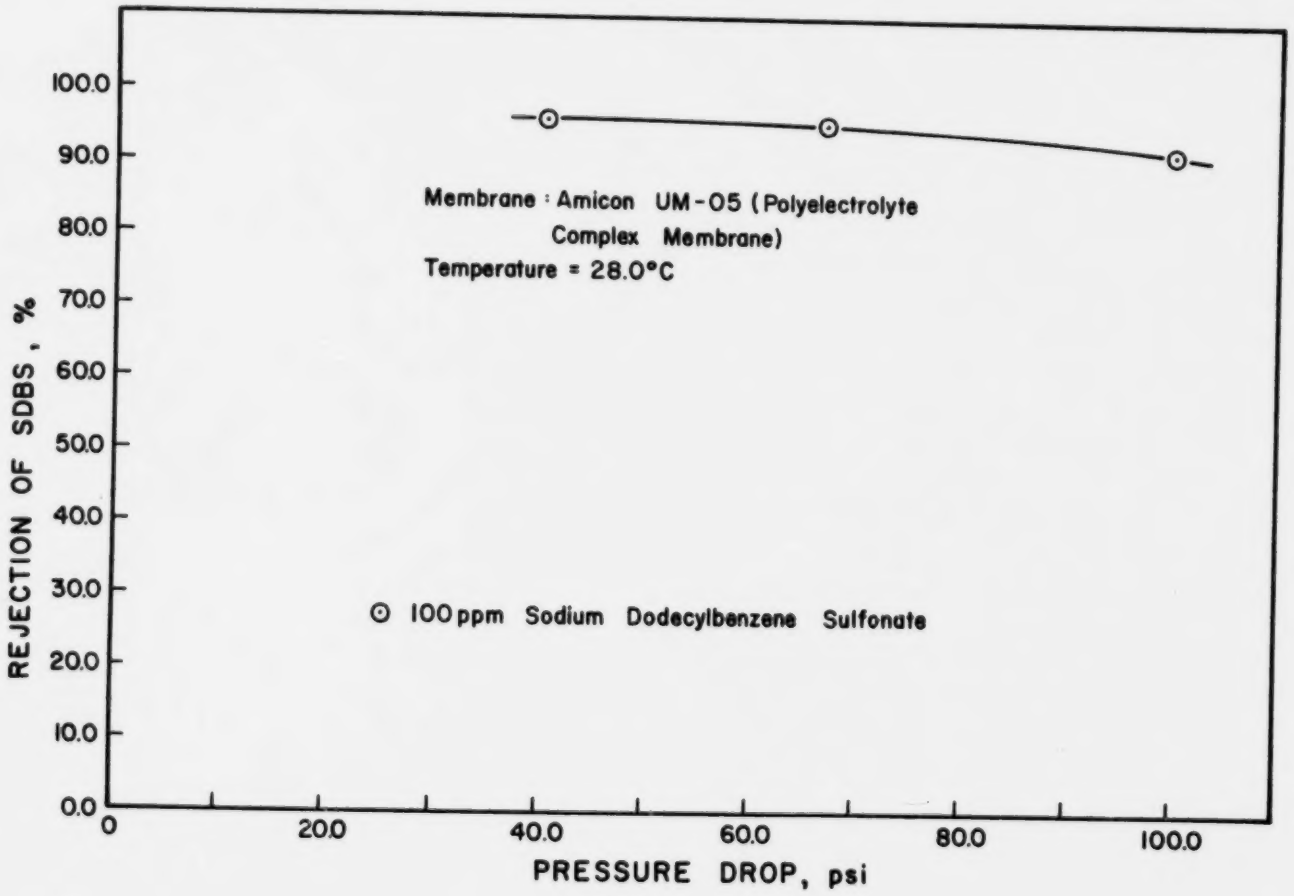
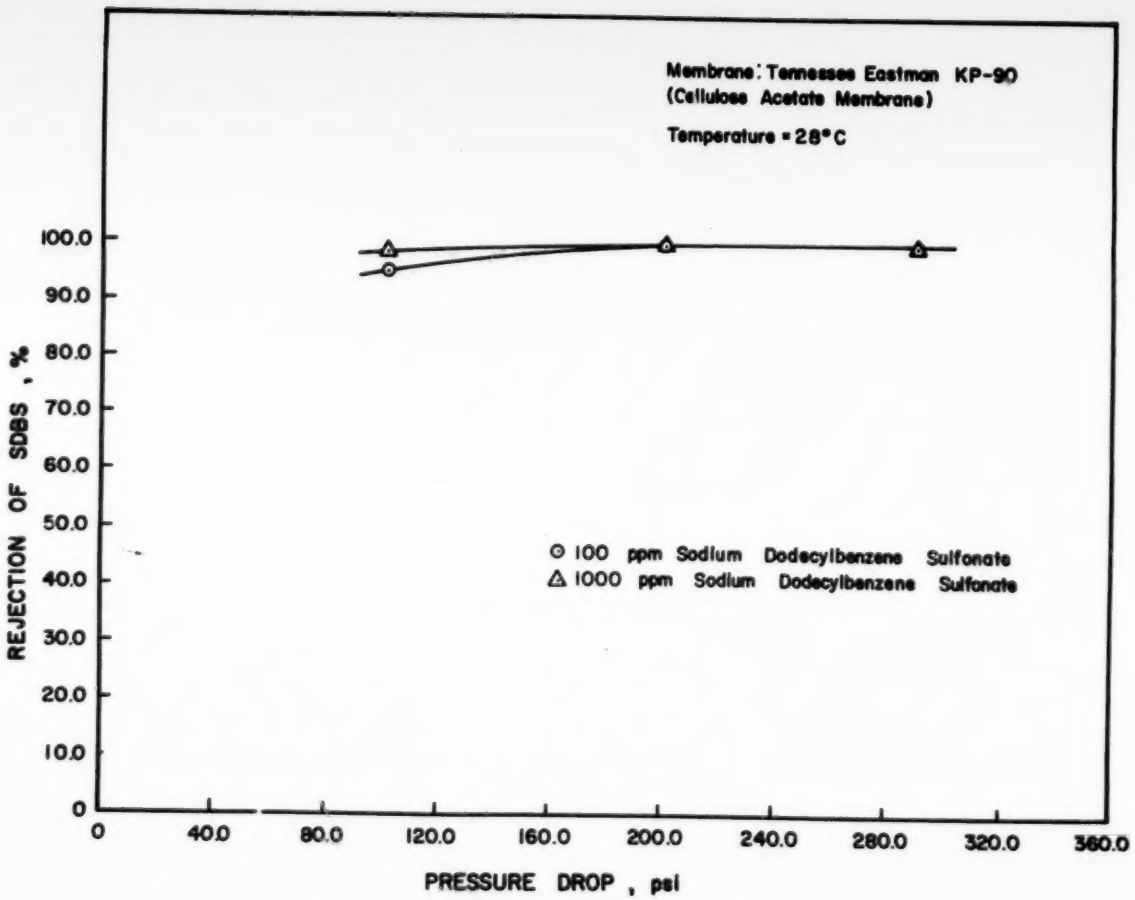

100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
REJECTION OF SDBS, %
0
20.0
40.0
60.0
80.0
100.0
PRESSURE DROP, psi
Membrane : Amicon UM-05 (Polyelectrolyte Complex Membrane)
Temperature = 28.0°C
⊙ 100 ppm Sodium Dodecylbenzene Sulfonate

Fig. 12. Effect of sodium dodecylbenzenesulfonate on the solute rejection by a cellulose acetate membrane


Membrane: Tennessee Eastman KP-90
(Cellulose Acetate Membrane)
Temperature = 28°C
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
REJECTION OF SDBS , %
⊙ 100 ppm Sodium Dodecylbenzene Sulfonate
△ 1000 ppm Sodium Dodecylbenzene Sulfonate
0
40.0
80.0
120.0
160.0
200.0
240.0
280.0
320.0
360.0
PRESSURE DROP , psi

polarized state does not occur instantaneously, but rather takes place gradually over a range of experimental conditions. In fact, for some solute-membrane combinations the entire pre-gel-polarized state might be characterized by the formation of a "gel layer" which, in the pressure ranges in question, would be almost completely permeable to the solvent but would effectively act as a partial barrier to passage of the much larger solute molecules. Another possibility is that of gradual micelle formation, as discussed in a previous section. The present data are inadequate to establish the validity or invalidity of any of these possibilities, however, and so further discussion of this point is deferred until additional tests are performed.

In the duplicate tests run following rinsing of the membranes, all percentage solute rejections were within 4% of the original data, and in most cases the deviations were closer to 1%.

Results for Flux and Solute Retention of Carbowax 600 Solutions

Flux and rejection data for the ultrafiltration of Carbowax 600 solutions with both the cellulose acetate membrane and the polysalt membrane are shown in Figures 13 through 16. Carbowax 600 is Union Carbide Corporation's trade name for an approximately 600 molecular weight poly(ethylene oxide). Carbowax 600 has a comparable molecular weight to Triton X-100 but owing to its molecular symmetry does not exhibit surface activity.

In general there was no significant flux reduction associated with the presence of Carbowax 600 in the ultrafiltration feed. Solute retention changed only slightly as the concentration of Carbowax 600 or the transmembrane pressure drop increased.

The product flux for the Carbowax 600 - cellulose acetate membrane combination, both for the 100 ppm and the 1000 ppm solution, was essentially the same as the distilled water (no solute) flux. In fact the addition of 100 ppm Carbowax 600 resulted in a slight flux increase over the distilled water flux. At this low concentration, Carbowax 600 may exhibit a plasticizing effect on the membrane matrix, thereby "opening" the membrane structure and, therefore, increasing the flux. At 1000 ppm of Carbowax 600, the slight flux reduction ranged from 0% at ΔP = 100 psi to 7% at ΔP = 290 psi.

For both solute concentrations, solute retention by the cellulose acetate membrane was essentially independent of the pressure drop, but the retention decreased slightly as the Carbowax 600 concentration increased from 100 ppm to 1000 ppm. Since Carbowax 600 is a nonsurfactant and incapable of forming aggregated or micellar particles, this result is consistent with the concept of micelle formation postulated in con-

Fig. 13. Effect of Carbowax 600 concentration on the trans-membrane flux through a cellulose acetate membrane

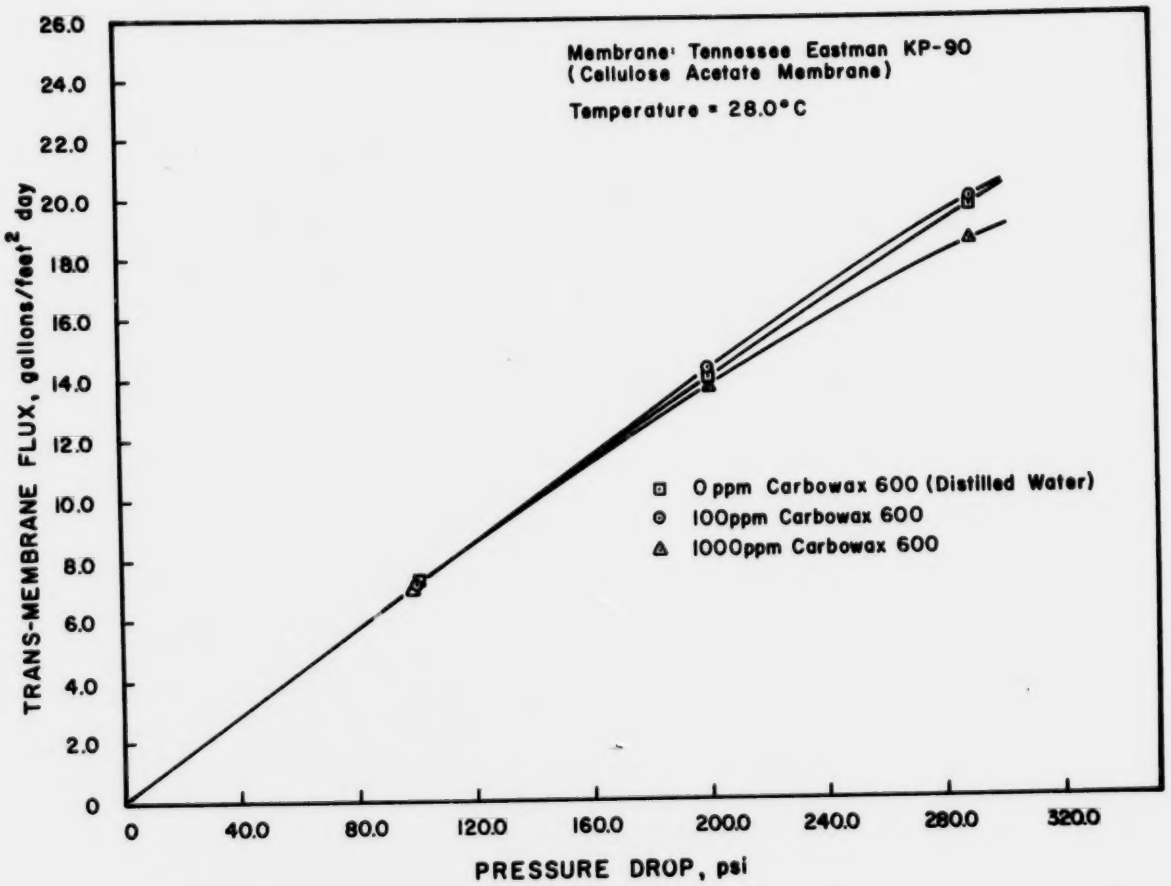
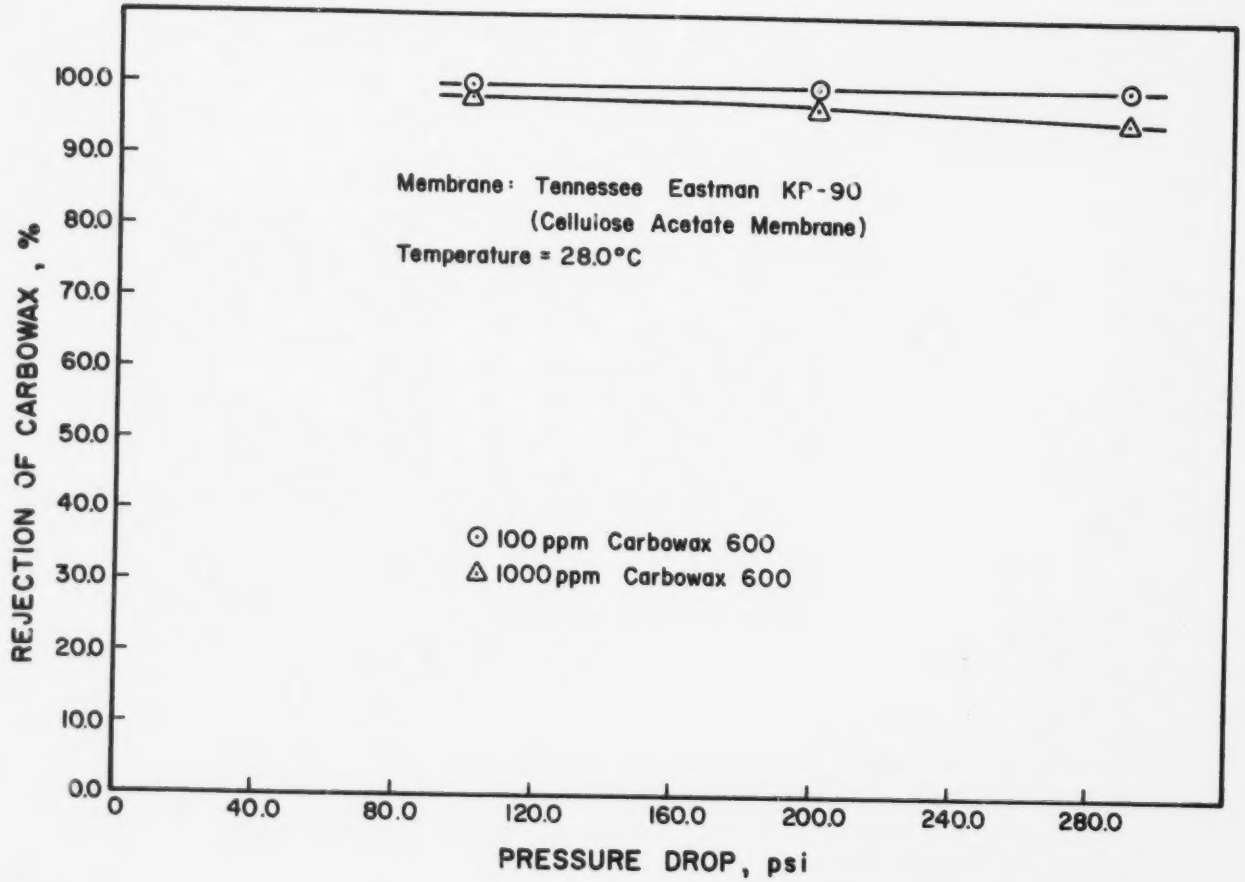

Membrane: Tennessee Eastman KP-90
(Cellulose Acetate Membrane)
Temperature = 28.0°C
0 ppm Carbowax 600 (Distilled Water)
100ppm Carbowax 600
1000ppm Carbowax 600
TRANS-MEMBRANE FLUX, gallons/feet² day
PRESSURE DROP, psi
0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
22.0
24.0
26.0
0
40.0
80.0
120.0
160.0
200.0
240.0
280.0
320.0

Fig. 14. Effect of Carbowax 600 concentration on the solute rejection by a cellulose acetate membrane


100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
REJECTION OF CARBOWAX , %
Membrane: Tennessee Eastman KP-90
(Celluiose Acetate Membrane)
Temperature = 28.0°C
⊙ 100 ppm Carbowax 600
△ 1000 ppm Carbowax 600
0
40.0
80.0
120.0
160.0
200.0
240.0
280.0
PRESSURE DROP, psi

nection with the observed rejection of Triton X-100.

For the polysalt membrane only a slight flux reduction can be attributed to the addition of 100 ppm Carbowax 600. The flux decline varied from 6% at ΔP = 40 psi to 1% at ΔP = 100 psi. At 1000 ppm of Carbowax 600 the flux reduction was essentially independent of pressure drop, remaining constant at about 8%. Although these curves suggest that there is a measurable flux reduction associated with the addition of Carbowax 600 to a distilled water feed, these reductions are much smaller than those associated with surfactant feeds.

As the pressure drop increased, solute retention for the 100 ppm Carbowax 600 - polysalt membrane combination decreased slightly while the retention of Carbowax 600 from the 1000 ppm solution went through a minimum as pressure drop was increased. Retention by the polysalt membrane decreased slightly as the Carbowax 600 concentration increased from 100 ppm to 1000 ppm.

All of the observed flux reductions associated with Carbowax 600 solutions were found to be reversible consequent to a distilled water rinse. The original pure solvent flux measured prior to ultrafiltration of solute containing solutions was re-established consequent to rinsing. In addition, duplicate tests with the same membranes used for the original runs were performed at random only for the Carbowax 600 - cellulose acetate membrane combination. In these tests the measured fluxes were within 3% of their values in the first set of runs, and the measured solute retentions were within 0.3% of the originally obtained data.

Importance of Molecular Asymmetry in Flux-Limiting Solute-Membrane Interactions

Since the nonsurfactant, Carbowax 600, and the surfactant, Triton X-100, are molecular analogs, except for the molecular asymmetry of the Triton X-100, the different effects of these two solutes on the trans-membrane flux, as shown in Figures 17 and 18, characterize the contribution of molecular asymmetry and therefore surface activity to flux-limiting solute-membrane interactions. As shown previously, the trans-membrane flux may be described in terms of a series of hydraulic resistances including the membrane, the gel layer, the concentration boundary layer, and specific solute-membrane interactions. This result is shown by Eq. 29;

$$J_1 = \frac{\Delta P}{R_m + R_g + R_p + R_i} \qquad (29)$$

For the case of distilled water transport only the membrane resistance, R_m, is operative. Presumably, the Carbowax 600 would not interact with the membrane giving rise to an additional resistance, R_i. In fact, the

Fig. 15. Effect of Carbowax 600 concentration on the trans-membrane flux through a polysalt membrane

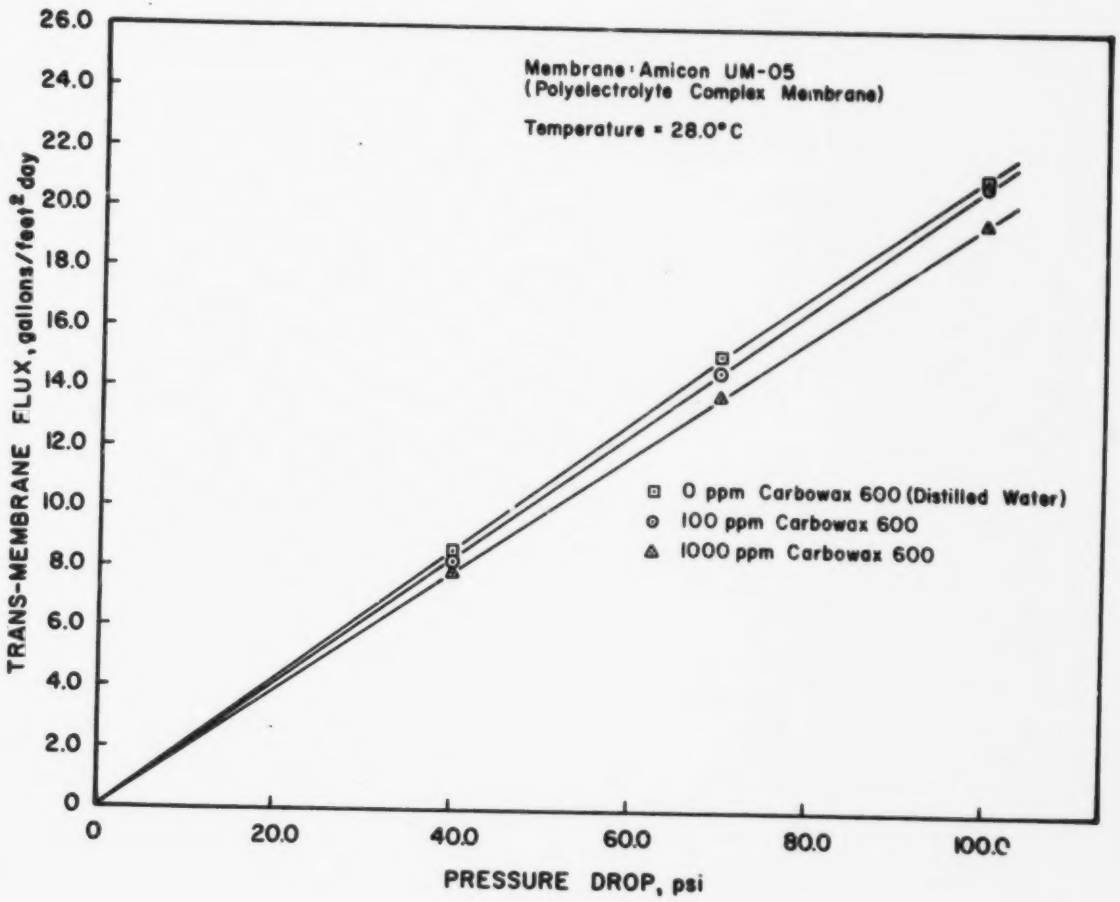
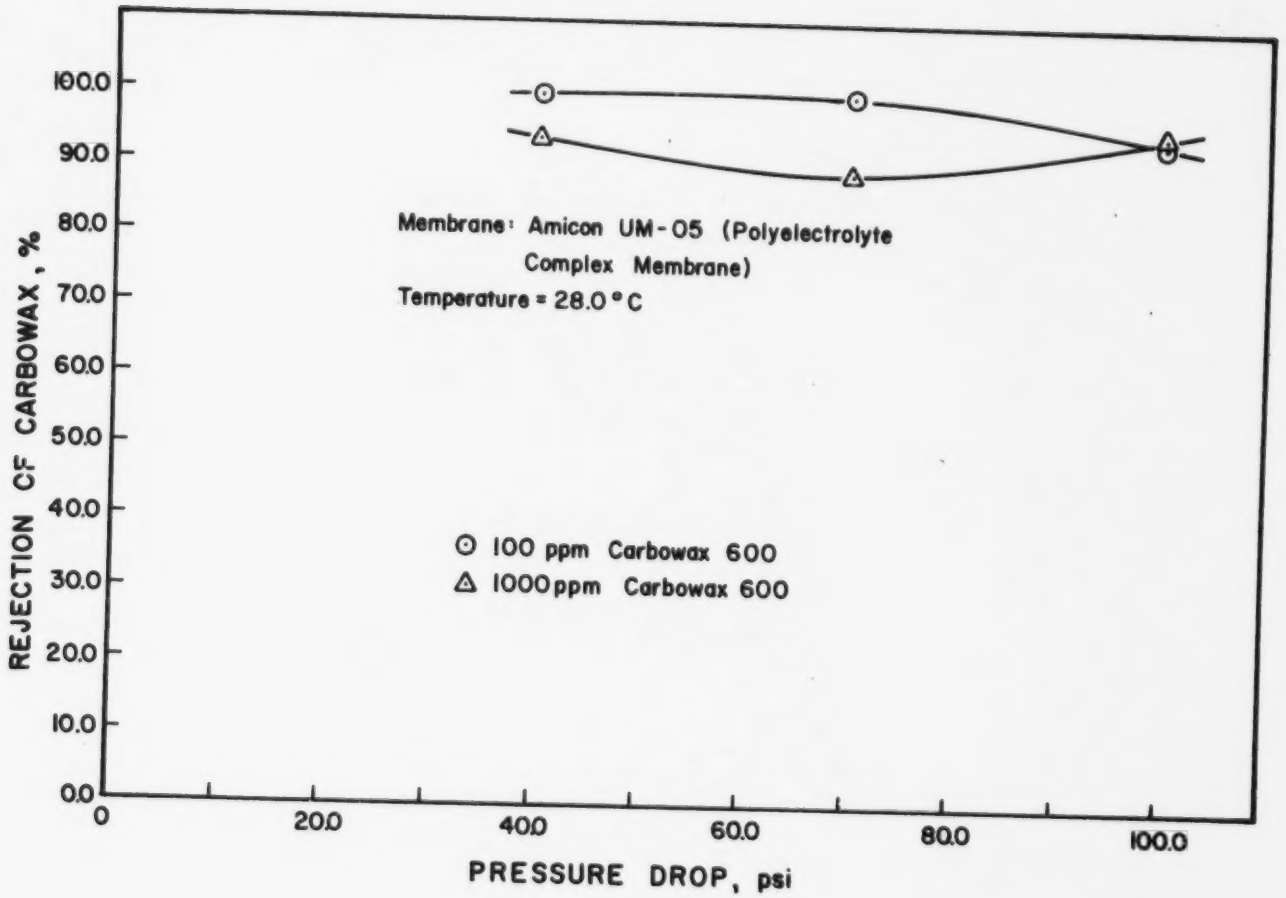

Membrane : Amicon UM-05
(Polyelectrolyte Complex Membrane)
Temperature = 28.0°C
0 ppm Carbowax 600 (Distilled Water)
100 ppm Carbowax 600
1000 ppm Carbowax 600
TRANS-MEMBRANE FLUX, gallons/(feet)² day
PRESSURE DROP, psi
26.0
24.0
22.0
20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0
0
20.0
40.0
60.0
80.0
100.0

Fig. 16. Effect of Carbowax 600 concentration on the solute rejection by a polysalt membrane


100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
REJECTION OF CARBOWAX, %
0
20.0
40.0
60.0
80.0
100.0
PRESSURE DROP, psi
Membrane: Amicon UM-05 (Polyelectrolyte Complex Membrane)
Temperature = 28.0 °C
⊙ 100 ppm Carbowax 600
△ 1000 ppm Carbowax 600

data of Figure 17 suggest that only the membrane resistance contributes to the rate determining step controlling the ultrafiltration of Carbowax 600 through cellulose acetates. It is reasonably assumed, therefore, that the flux decline observed for the Triton X-100 solutions is a consequence of specific membrane interactions accruing from surface activity and that analogous to the observed behavior with Carbowax 600, the values of R_g and R_p are indeed zero for the Triton X-100 ultrafiltration under the imposed experimental conditions. The observed flux decline is solely a consequence of the solute-membrane interactions modeled by the term, R_i.

Comparisons involving the polysalt membrane are presented in Figure 18. Only at ΔP = 100 psi does there appear to be any flux-limiting effect attributable directly to molecular asymmetry.

Fig. 17. Comparison of the effects of Carbowax 600 and Triton X-100 concentrations on the trans-membrane flux through a cellulose acetate membrane

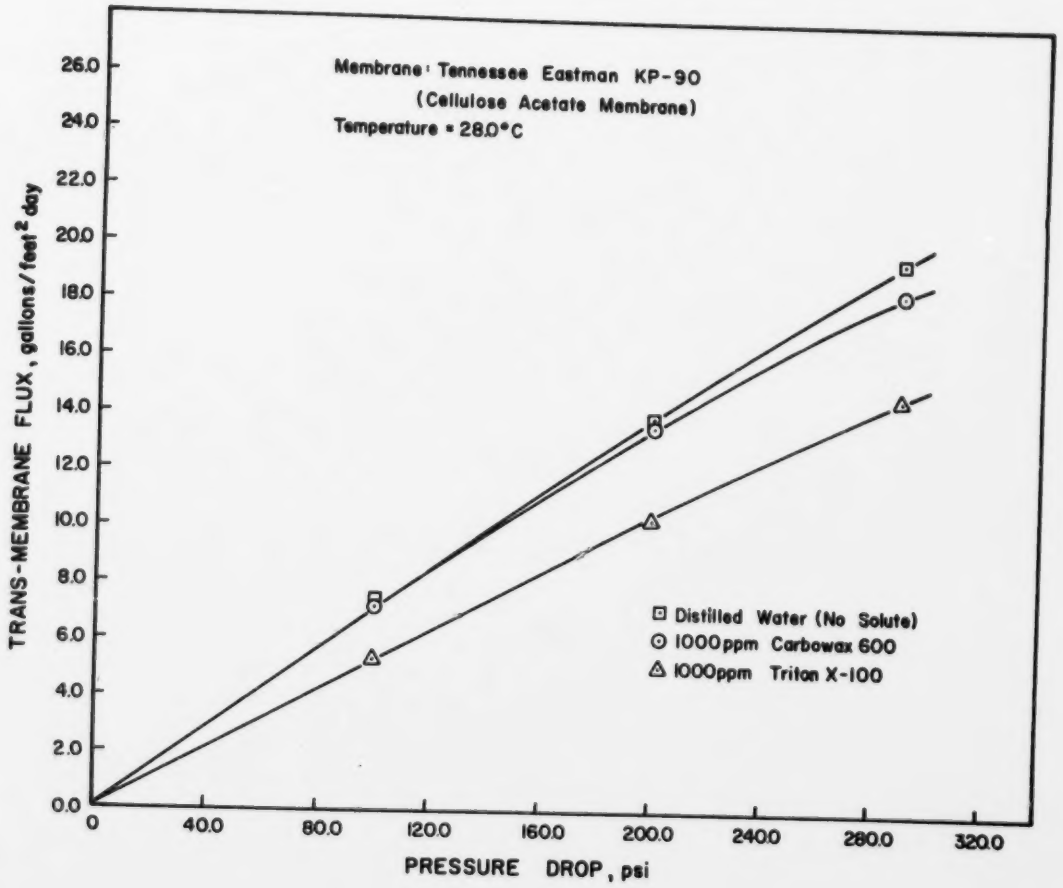
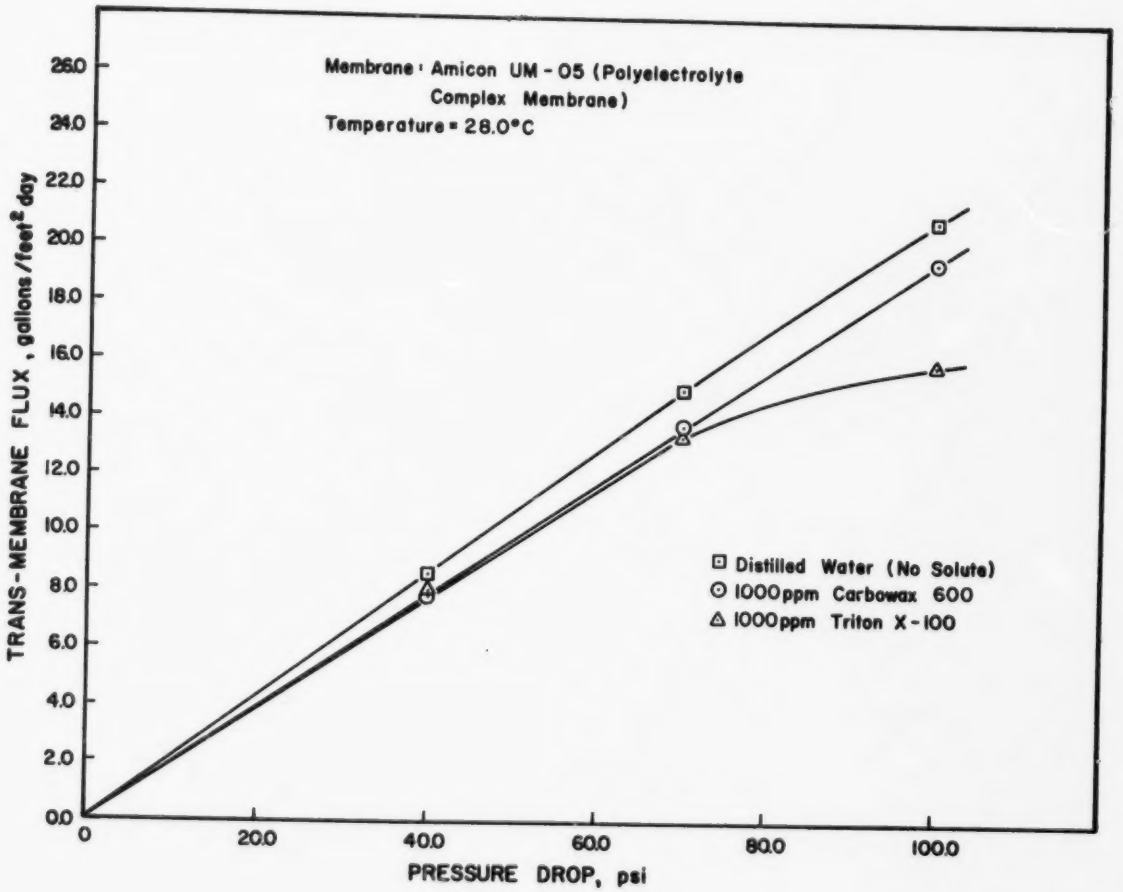

Membrane: Tennessee Eastman KP-90
(Cellulose Acetate Membrane)
Temperature = 28.0°C
TRANS-MEMBRANE FLUX, gallons/feet² day
PRESSURE DROP, psi
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
22.0
24.0
26.0
0
40.0
80.0
120.0
160.0
200.0
240.0
280.0
320.0
Distilled Water (No Solute)
1000ppm Carbowax 600
1000ppm Triton X-100

Fig. 18. Comparison of the effects of Carbowax 600 and Triton X-100 concentrations on the trans-membrane flux through a polysalt membrane


Membrane : Amicon UM - 05 (Polyelectrolyte Complex Membrane)
Temperature = 28.0°C
TRANS-MEMBRANE FLUX, gallons/feet² day
26.0
24.0
22.0
20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
0
20.0
40.0
60.0
80.0
100.0
PRESSURE DROP, psi
Distilled Water (No Solute)
1000ppm Carbowax 600
1000ppm Triton X-100

SECTION VII

ACKNOWLEDGMENTS

Mr. J. A. Palmer performed the experimental work in partial fulfillment of the requirements for the degree of Ph.D. in chemical engineering. Mr. D. F. Carey assisted in the construction of the ultrafiltration test loop. Professor R. M. Felder, Department of Chemical Engineering, North Carolina State University, assisted in the design and analysis of the experimental program. Dr. W. W. Lanier of Chemstrand Research Center (Research Triangle Park, North Carolina) developed a simple analytical technique for quantitative determinations of Carbowax 600 in distilled water.

The cooperation and contributions of Mr. Palmer, Mr. Carey, Professor Felder, and Dr. Lanier are gratefully acknowledged.

The support of Eastman Chemical Products, Inc. (Kingsport, Tennessee) in supplying cellulose acetate membranes is gratefully acknowledged.

The support of Rohm and Haas (Philadelphia, Pennsylvania), Union Carbide Corp. (New York, New York), and Cities Service Company (Atlanta, Georgia) in supplying test solutes is gratefully acknowledged.

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SECTION VIII

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SECTION IX

PUBLICATIONS AND PATENTS

As a result of this research a paper entitled "Effects of Surfactants in Flux-Limiting Concentration Polarization in Ultrafiltration Processing" and authored by J. A. Palmer, H. B. Hopfenberg, and R. M. Felder was presented to the Symposium on Processing of Liquid Wastes in the Food Industry, Part II Membrane Processes at the Seventy-Second National Meeting of the American Institute of Chemical Engineers, St. Louis, Missouri, May 21-24, 1972.

This paper has been submitted for publication to the Journal of Colloid and Interfacial Science.

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SECTION X

NOMENCLATURE

$\bar{C}_1$ = Mean concentration of solvent in the membrane (g/cm^3)

C_2 = Solute concentration (g/cm^3)

C_b = Solute concentration in bulk upstream solution (g/cm^3)

C_g = Gel solute concentration (g/cm^3)

C_p = Solute concentration in permeate (g/cm^3)

C_w = Solute concentration at the upstream membrane wall (g/cm^3)

D_1 = Solvent diffusion coefficient in the membrane (cm^2/sec)

D_2 = Solute diffusion coefficient in the membrane (cm^2/sec)

D_s = Solute diffusion coefficient in the concentration boundary layer (cm^2/sec)

d = Particle diameter (cm)

J_1 = Trans-membrane solvent flux (ml/cm^2-sec)

J_2 = Trans-membrane solute flux (ml/cm^2-sec)

k_2 = Solute distribution coefficient between the membrane and the solution ($ml/psi-cm^3$)

k_s = Solute mass transfer coefficient, defined as D_s/δ (cm/sec)

M = Concentration polarization modulus, defined as C_w/C_b (dimensionless)

$\bar{P}_1$ = Membrane permeability constant for the solvent (ml/cm-sec-psi)

$\bar{P}_{1g}$ = Gel-layer permeability constant for the solvent (ml/cm-sec-psi)

$\bar{P}_{1p}$ = Concentration-boundary-layer permeability constant for the solvent (ml/cm-sec-psi)

$\bar{P}_2$ = Membrane permeability constant for the solute (ml/cm-sec-psi)

ΔP = Trans-membrane pressure drop (psi)

R = Gas constant ($psi-cm^3/mole°K$)

R_g = Flux resistance of the gel layer (psi-cm^2-sec/ml)

R_i = Flux resistance due to the specific solute-membrane interactions (psi-cm^2-sec/ml)

R_m = Flux resistance of the membrane (psi-cm^2-sec/ml)

R_p = Flux resistance of the concentration boundary layer (psi-cm^2-sec/ml)

T = Absolute temperature (°K)

t_g = Thickness of the gel layer (cm)

t_m = Membrane thickness (cm)

$\bar{V}_1$ = Partial molar volume of the solvent in solution (cm^3/mole)

X = Distance perpendicular to the membrane surface (cm)

δ = Concentration boundary layer thickness (cm)

ε = Porosity of the gel layer (dimensionless)

$\Delta\Pi$ = Solute osmotic pressure difference between the bulk upstream solution and the permeate solution (psi)

ρ_1 = Density of solvent (g/ml)

σ = Solute rejection coefficient

σ_a = Apparent solute rejection coefficient